IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 29, 1988

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Group Art Unit: 115 : Examiner: Dennis Albrecht

FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF ALBERT M. TORRESSEN
WITH RESPECT TO HIGH Tc SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Albert M. Torressen, hereby declare and say that:

1. I joined the International Business Machines Corporation (IBM Corp.) on June 12, 1978, and began my employment as a laboratory technician at the Thomas J. Watson Research Center, Yorktown, New York. In 1986, I was a senior lab specialist at the Watson Research center, and reported to Dr. Stephan von Molnar. My specialty has been measurement of thermal and transport properties of a material including, for example, measurements of heat capacity, resisitivity, and Hall coefficients. Generally, these are dynamic measurements which serve to charactize a material.

2. On approxmately October 22, 1986, Richard L. Greene approached Stephan von Molnar to enlist his assistance in obtaining specific heat measurements of samples which he said were new superconducting materials that had been recieved from Georg Bednorz and Alex Mueller of IBM's Zurich research laboratory. These were ceramic oxide materials comprised of Ba-La-Cu-O. In turn, von Molnar asked me to assist Greene in making these measurements, since I had expertise in the use of the apparatus and had done similar measurements for many years. I began to calibrate the apparatus and to prepare for specific heat

measurements at that time, and worked continuously on a daily basis, from about October 22, 1986 through the remainder of 1986 and into 1987 on these measurements. Richard L. Greene was in the laboratory during these measurements and supervised the experimentation, relying on my expertise with respect to the apparatus. Later, we analyzed the data together.

3. Richard Greene wanted to do specific heat measurements of these superconducting samples. Such measurements are used to dertermine if a material is a superconductor and also to tell how much of the material is superconducting. In general, the specific heat of the apparatus is first carefully measured using a bolometer in order to provide background specific heat and to calibrate the apparatus. After this, the actual sample to be measured is attached to the bolometer and the specific heat of the entire apparatus, including the sample, is again measured. When the background specific heat (due to the bolometer) is subtracted, the specific heat of the sample can be determined. This is done over a temperature range, in our measurements 2-50K, in order to obtain a plot of specific heat versus temperature for the sample being measured. This is a dynamic measurement in which we look at how the heat in the sample decays as a function of time through a known heat leak and from that extrapolate via a computer program specific heat versus temperature. This is a known procedure that is done in many laboratories.

4. The commercial bolometer that Greene and I used to measure the specific heat of these superconducting Zurich samples was comprised of an insulating aluminum oxide on which strips of RuO_2 were evaporated. Electrical contacts were made to the RuO_2 strips, each strip having two AuCu wires attached thereto which were in turn connected to an ambient temperature control (about 2K). A heat pulse was then applied to the bolometer and its temperature decay versus time was measured. This was done over the aforementioned temperature range in order to get background specific heat and to calibrate the apparatus. Generally, it takes us about two days to measure the background specific heat in order to prepare for the actual specific heat measurements of the sample. Measurement of each sample also takes about two days, so approximately four days represents the total time required for each measurement. This is based on full time activity.

5. Prior to making the specific heat measurements, the samples are prepared. The superconducting oxide samples received from Bednorz and Mueller were pellet samples which were then cut into slices by a diamond wheel. I believe that this was done by Richard Greene. To make the specific heat measurements, a sample having a mass of about 20 mg is required, it being desirable to have a flat surface sufficient to provide good thermal contact. In the calculation of specific heat, the weight (mass) of the sample is factored into the equation. Also, I made specific checks of the measuring apparatus throughout this time period (October 22, 1986 - February, 1987) and I made continual checks on the measuring apparatus in order to ensure its calibration. All of the data collected during the measurements was also provided to a personal computer that was interfaced to the apparatus. In this manner, a computer printout of all of the measurements was available.

6. Exhibit A attached hereto is comprised of copies of eight pages of my laboratory notebook and a copy of the notebook cover entitled "Specific heat - Zurich oxide - 10/21/86". All of the writing of these pages was entered by me on the dates indicated on the pages. These pages are true copies of the corresponding pages of my laboratory notebook that I have numbered in red in the upper right hand corner to enable discussion of the data on each page. As I mentioned previously, background specific heat and calibration of the instrumentation was done prior to mounting the sample and measuring the specific heat of the sample. For example, the data on the top two-thirds of page one shows the measured data for the calibration and background measurements. The bottom of this page indicates the specific heat data that was obtained October 27, 1986 when the sample was mounted on the RuO_2 bolometer. The weight of the sample is also mentioned, the sample being designated "BLCO 2 - I". This stands for Ba-La-Cu-O ceramic superconductor. I noted that it was a "multi-phase sample" which is not a particular good choice for a specific heat measurement. Generally, the data is more clean and easy to interpret if the sample contains only a single phase. Measurements on the apparatus and with this particular sample continued on October 28 and 29, 1986, the data that Greene and I obtained being listed on page 2 on Exhibit A.

7. On November 3, 1986 we used a new sample, in this case the sample designated "BLCO 21 -II". We used a new calibration of the bolometer and then mounted the sample on the bolometer to take the data, which was obtained on November 4, 5, 6, 1986. The data for this sample measurement is contained on pages 4 and 5 of Exhibit A, where it is noted that this is a single phase sample. Additional data is also contained on page 6 of Exhibit A.

8. Richard Greene and I analyzed this data between about November 10 and November 19, 1986. At that time, the samples showed only a very small (1 - 2 percent) anomaly at the transition temperature, which was sufficiently small that no obvious bump occurred in this specific heat data. Because these materials had a very broad transition in resistivity versus temperature, such a very small effect was expected.

9. On or about November 19, 1986, the apparatus was changed slightly by installing a capacitor and mounting a magnet on the specific heat cryostat. The instrument was then recalibrated and measured, the data of this being shown on page 7 of Exhibit A. A capacitance bridge was used to control temperature as noted on page 8 of Exhibit A which showed further data taken on the instrumentation. After this time, we continued to take specific heat measurements of additional samples of the Ba-La-Cu-O oxide superconductors obtained from Bednorz and Mueller.

10. Exhibit B is a true copy of pages of a printout from the personal computer that was interfaced with the apparatus used to make the aforementioned specific heat measurements. These pages illustrate the background measurements and calibration of the instrumentation, as well as the data that were obtained when the sample was mounted on the bolometer. Additionally, many plots are included in this Exhibit which are plots of the data that were measured. Specific heat measurements of the samples are plotted where the samples are designated either "Zurich oxide" or "ZO". Sometimes the sample is also designated "Zurich oxide BLCO, etc." In December, 1986, additional samples were obtained from Bednorz and Mueller, these new samples containing Sr instead of Ba. They are designated "SLCO", which represents Sr-La-Cu-Oxide. The heat capacity of these samples was also measured, as represented by the plot dated January 9, 1987. Measurements were made in the absence of and in the presence of an applied magnetic field H. Sometimes the plots show

the sample plus the designation "BG". This indicates that background was also present in the measurement.

11. The data that we obtained during our specific heat measurements are representative of the type of data which we now obtain on refined samples of these superconducting copper oxide materials. At the time we made our initial measurements in 1986, we were somewhat puzzled by the small vertical offset that occurred for temperatures extrapolated from 2-0K. However, such offsets have been found to be a characteristic of the superconducting copper oxides of the type first discovered by Bednorz and Mueller.

12. In addition to his specific heat measurements, Richard Greene also measured resistivity versus temperature in the presence of a magnetic field, for these Ba-La-Cu-O samples. This was done in my lab, and I explained my experimental instruments and set-up to Greene. I observed Richard Greene making these measurements and saw the shift in resisitivity versus temperature curve with an applied magnetic field. This shift clearly indicated the superconducting nature of these samples at temperatures in excess of 30^{O}K. The measurements described in this paragraph occurred in the last week of November, 1986 and in the first week of December, 1986. These measurements and our specific heat measurements were part of our continuous daily effort, from about October 22, 1986 to establish the superconductive properties of these samples above 30^{O}K. I recall these measurements clearly and remember Richard Greene asking me how to better stabilize the sample temperature while the applied magnetic field was changed in amplitude.

13. In addition to the acts described hereinabove relating to work done by Richard Greene and by me, I was aware of the work being done by Chang C. Tsuei to measure resistivity versus temperature for these Ba-La-Cu-O superconducting samples. I was present in the laboratory with Chang C. Tsuei and and Sung Il Park during their measurement of at least one of these samples, and saw the hardcopy of a resistivity versus temperature plot developed by the xy recorder connected to their measurement apparatus. This plot showed the onset of superconductivity at approximately 35K followed by a broad transition to zero resistivity. I knew the nature of their experimentation and understood the data. This

measurement and my observation occurred approximately the first week of November, 1986.

14. My recollection of the events described hereinabove is vivid, as there was great excitement about the importance of the discovery of new superconducting materials by Bednorz and Mueller. Because of this, activity continued on a daily basis, both morning and evening, to characterize these materials in coordination with Bednorz and Mueller.

15. All acts referred to hereinabove performed by myself, Richard L. Greene, Chang C. Tsuei, and Sung Il Park occurred in the United States.

16. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

Albert M. Torressen
ALBERT M. TORRESSEN

DATE: 31 March 1988

TORRESEN
EXHIBIT A

National

College Ruled White Paper

Single Subject

10/2?/86

Do calibrations and Background Specific Heat

0216HTCA.DAT (5-33°K) } RuO2 Calibrations
0216HTCB.DAT (28-40°K) }

0226BGHD.DAT (6-40°K) Background Decay.
→ Bol.+Wires+Grease

0226BGHE.DAT (6-10°K)
0226BGHF.DAT (6-15°K)
0226BGHG.DAT (6-25°K)

0226BGHH.DAT (10-20°K)
0226BGHI.DAT (10-40°K)

0226BGHJ.DAT (20-40K)

10/23/86

0236PCH.DAT ($T_0 = 6°K$, Power Calibration to 40°K)
TXT 0236LTC.DAT (Temperature Calibration 2-12°K)
~~TXT~~ 0236PCL.DAT ($T_0 = 2°K$, PC to 11°K)
TXT 0236BGL.DAT ($T_0 = 2°K$, 2-11°K BG)

10/27/86

Sample put in — BLCO2-I — Multiphase sample (bad choice

Weight 25.66 ± 0.1 mg

0276PCH.DAT ($T_0 \simeq 24K$, Power Calib. to ~50K)
→ Block 186.35Ω ≃ 24K Carbon Glass TC

0276 ~~BGH~~ ZOHA.DAT (Decay 35-24K)
0276ZOHB.DAT (Decay 40-24K)

10/28/86

Run Some More Cv Data & Power Calibrations

TXT 0286PCL.DAT (PC 2-8K) Power Calibration (PC)
TXT 0286ZOLA.DAT (Decay 2-8K)

TXT 0286ZOHA.DAT (Decay 12-5K)
TXT 0286PCA.DAT (PC 5-12K)

TXT 0286ZOHB.DAT (Decay 20-10K)
TXT 0286PCB.DAT (PC 10-20K)

TXT 0286ZOHC.DAT (Decay 28-18K)
TXT 0286PCC.DAT (PC 28-17K)

~~Tomorrow – look for jump in C with ac method~~
~~– compile & analyze data~~

~~[illegible] bandwidth T controller when setting up PC & Decay Runs~~

~~Check how Absolute value of [illegible] data agrees [illegible]~~

10/29/86

TXT 0296HTC.DAT – Bolometer Calib at HT (28-50 K)

TXT 0296ZOHA.DAT (Decay 30-24K)
TXT 0296ZOHB.DAT (Decay 33-24K)
TXT 0296ZOHC.DAT (Decay 37-24K) → C.DAT file changed now a 43-24 decay
TXT file ok (37-24)
0296ZOHD.DAT (Decay 43-24K) 300 ms τ
0296ZOHE.DAT (Decay 43-24K) → 1 sec τ

11/3/86

New Sample + Background — hopefully single ~~phase~~ sample this time
BLC021-II

Start with background + new bolometer calibration

Using 116 preamp on PAR — noise greatly reduced (see curves)

TXT } NØ36HTCA.DAT (5-~~32~~K) RuO_2 calibration
TXT } NØ36 HTCB.DAT (2~~6~~-40K) "

TXT NØ36BGHA.DAT (Decay 15-5K)
TXT NØ36PCHA.DAT (Power Calib 5→15K)

~~NØ36BGHB.DAT (Decay 25-12K)~~

11/4/86

Pump to ~2K and do LT runs

TXT } NØ46LTCA.DAT (2-10K) RuO_2 Calibration
maybe O not Ø it is

TXT NØ46BGLA.DAT (Decay ~8-~~2~~K 1.8) → seemed to have long decay at end → might be base T raising slightly with current on?

TXT } NØ46BGLB.DAT (Decay ~8-2K) → Rerun with diff base T — still seem to see drift — but smaller

TXT } NØ46PCLA.DAT (Power Calib. ~~15~~ 2 - 8K) → Same base as Run BGLB Decay

Back to 4.2K Bath

TXT NØ46BGHA.DAT (Decay 25-12K)
TXT NØ46PCHA.DAT (Power Calib 12-25K) → Look at the data (need to redo) the beginning
TXT NØ46PCHB.DAT (rerun of HA) → * better — use this one

TXT NØ46BGHB.DAT (Decay 35-20K)
TXT } NØ46PCHC.DAT (Power Calib. 20-35K)

11/6/86

Put on New sample BLCO 21-II Weight 14.82 mg
(Single Phase) ±.02 mg

$\boxed{2, 5, 12, 20 \text{ set T's}}$

CGlass	Bol V
5k	9.1300
12k	3.434
20k	8.113
	8.076

didn't put into computer

NΦ66ZOHA.DAT (Decay 15-5 K) 30ms?

TXT NΦ66ZOHB.DAT (Same 15-5K with T=100ms)

TXT NΦ66ZOHC.DAT (Decay 25-12K) T=180ms

TXT NΦ66ZOHD.DAT (Decay 35-20K) T=100ms

~~NΦ66ZOHE.DAT~~

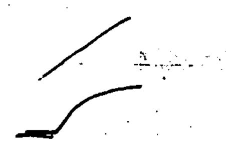
✓ TXT NΦ66HTCA.DAT (Bol. Calibration 5-32K)

✓ TXT NΦ66HTCB.DAT (Bol. Calibration 20-40K)

TXT NΦ66ZOHE.DAT (Decay 33-5K) T=100ms

✓ TXT NΦ66ZOHF.DAT (Decay 12-6K) T=100ms

✓ TXT NΦ66ZOHG.DAT (same decay but put in front of curve)



✓ TXT NΦ66ZOHH.DAT (Decay 24-6K)

✓ TXT NΦ66ZOHI.DAT (Decay 35-6K)

✓ TXT NΦ66PCHA.DAT (Power Calib 6-35K)

11/7/86

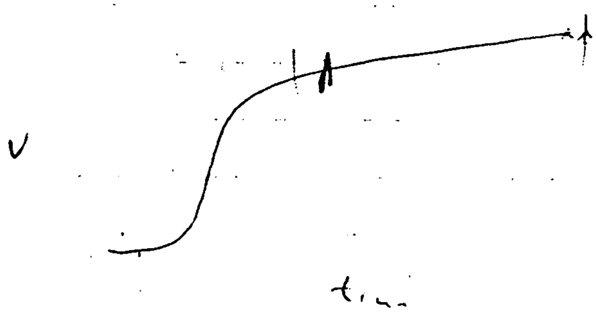
Go to LT

TXT { NΦ76LTCA.DAT (T calib 2-10K)

TXT NΦ76ZOLA.DAT (Decay 10-2K)

TXT NΦ76ZOLB.DAT (Same decay - more pts before end)

TXT NΦ76PCLA.DAT (Power Cal. 2-10 K)



Nov 10

m7WS10 SHEAT
Background from Sep24)BG9246
SVMC3, SVMT3 (2-12°K)

Background from Nov4
CBG2K1, TBG2K1 (2-~~8~~°K)

Zurich oxide (BLCO21 + BGD)
CA6, TA6 (2-12°K)

Installed CS-401GR-B Capacitor 19 Nov. 1986
Mounted 5 Tesla magnet on Specific heat cryostat
Cooled overnight to lN_2 temperature

	RuO2	C2329	CS401	
~77°K	7.2611 v	120.7 Ω	6.341 nf.	(To Null set CSC400 @ 12.682 nf)
~4.2°K	9.2015	1027.2	4.867 nf (1.000)	(set to null @ 1.000 nf)

Raised temperature to 6°K with LR-130

				Bolo. (Power)	
~6°K	8.8762	600.1	(1.090 nf)	0	
	7.7308	"	1.140	540 μA	1.28043 v

N19620HA.DAT (6-32°K) Zero field
1.090 after decay

6°K	8.8765	600.1	(10.0918)	0	to control (using LR-130)
	8.8780	600.2	10.0882	0	" CSC400

11-20-86

Wired Persistent heat switch

~6°K	8.9830	601.5	(10.0882)	0	using CSC400

GAIN = 9
AUTORESET = OFF

Controlling @ ~6°K with Capacitance Bridge (CSC 400) (10.0880 nF)

11-21-86

	RU02	C2329	H	
	8.9224	606.1 (±0.3)	0	
	8.9214	605.9	5 mV (5A)	
	8.9204 (±.001)	605.9 (±1.0)	10 mV	
55 kG @	8.9197	605.8	20 mV	
636.7 G/A	8.9189	607.8	30 mV	
	8.9178	606.8	40 mV	
	8.9152	607.9	50 mV	
	8.9138	609.3	60 mV	
	8.9105	609.5	70 mV	70 A × 636.7 G/A = 44.5690 kG.

Change represents 0.025 K at 6 K H=0.

Changed over to LR-130 Controller since magnetoresistance of C2329 is small

~6°	8.8977	600.0	70 mV	0	
~32°	7.76	"	"	540 uA	1.2804 V

N216ZOHA.DAT (4.4 Tesla)

8.91	600.	0	0
7.76	"	"	540 uA

N21620HB.DAT (Zero Tesla)

25 mK @ 6.00

Calculate 70 mK @ 2.00 Possible change due to field.

TORRESSEN
EXHIBIT B

BkGd + Cr 3phase

Pt #	RUO2 VOLTS	C232 TEMP	SET TEMP	TEMP DEV
1	76.57E-01	27.98E+00	28.00E+00	0.100
2	76.38E-01	28.92E+00	29.00E+00	0.100
3	76.19E-01	29.91E+00	30.00E+00	0.100
4	76.00E-01	30.90E+00	31.00E+00	0.100
5	75.82E-01	32.08E+00	32.00E+00	0.100
6	75.65E-01	33.06E+00	33.00E+00	0.100
7	75.49E-01	34.03E+00	34.00E+00	0.100
8	75.33E-01	35.03E+00	35.00E+00	0.100
9	75.17E-01	36.06E+00	36.00E+00	0.100
10	75.02E-01	37.06E+00	37.00E+00	0.100
11	74.87E-01	37.90E+00	38.00E+00	0.100
12	74.72E-01	38.93E+00	39.00E+00	0.100

'Ctrl/⏎' to end, 'Ctrl/F1' to locate, or 'Cursor Keys' to scroll.

Pt #	RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
1	88.52E-01	49.80E-01	50.00E-01	0.050
2	86.92E-01	59.78E-01	60.00E-01	0.050
3	85.65E-01	69.79E-01	70.00E-01	0.050
4	84.62E-01	79.71E-01	80.00E-01	0.050
5	83.74E-01	89.67E-01	90.00E-01	0.050
6	82.99E-01	99.68E-01	10.00E+00	0.050
7	82.33E-01	10.98E+00	11.00E+00	0.050
8	81.72E-01	12.01E+00	12.00E+00	0.050
9	81.19E-01	13.01E+00	13.00E+00	0.050
10	80.74E-01	13.96E+00	14.00E+00	0.050
11	80.29E-01	14.99E+00	15.00E+00	0.050
12	79.89E-01	15.98E+00	16.00E+00	0.050
13	79.51E-01	16.97E+00	17.00E+00	0.050
14	79.16E-01	17.97E+00	18.00E+00	0.050
15	78.83E-01	18.97E+00	19.00E+00	0.050
16	78.53E-01	19.97E+00	20.00E+00	0.050
17	78.23E-01	20.97E+00	21.00E+00	0.050
18	77.94E-01	22.03E+00	22.00E+00	0.050
19	77.69E-01	22.97E+00	23.00E+00	0.050
20	77.45E-01	23.99E+00	24.00E+00	0.050

'Ctrl/⏎' to end, 'Ctrl/F1' to locate, or 'Cursor Keys' to scroll.

Pt #	RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
21	77.21E-01	24.97E+00	25.00E+00	0.050
22	77.00E-01	25.96E+00	26.00E+00	0.050
23	76.77E-01	26.97E+00	27.00E+00	0.050
24	76.56E-01	28.03E+00	28.00E+00	0.050
25	76.36E-01	29.00E+00	29.00E+00	0.050
26	76.16E-01	30.05E+00	30.00E+00	0.050
27	75.99E-01	31.00E+00	31.00E+00	0.050
28	75.82E-01	31.98E+00	32.00E+00	0.050
29	75.64E-01	32.96E+00	33.00E+00	0.050

'Ctrl/⏎' to end, 'Ctrl/F1' to locate, or 'Cursor Keys' to scroll.

Title: RUO2 VS TEMP PROGRAM
Run Id. - 0236LTC.DAT
Time and Date: 11:46:50 10-16-1986 - 12:48:13 10-16-1986
Parameter lines = 13
Min Temp to Plot = 01.00 K
Max Temp to Plot = 14.00 K
Min Volts to Plot = 8.00 Volts
Max Volts to Plot = 10.0 Volts
Plot Title = RUO2 VS TEMP
X Axis Plot Label = Sample Temp (K)
Y Axis Plot Label = RUO2 (Volts)
Start Temperature = 002 K
Temperature Step = 0.5 K
Temperature Stop = 014 K
LR400 Range = 20000 Ohms
Temperature Dev. = 0.050 K
Wait Time = 0010 seconds
Notebook messages = 4
RUO2 Calibration vs C2329 Carbon Glass Resistor
4 WIRE CONFIGURATION FOR BOLOMETER
BACKGROUND MEASUREMENT
STEPPING UP
Number of points = 21 Values per point = 4

Calibration

RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
99.26E-01	19.96E-01	20.00E-01	0.050
96.15E-01	25.17E-01	25.00E-01	0.050
94.16E-01	29.68E-01	30.00E-01	0.050
92.41E-01	34.72E-01	35.00E-01	0.050
91.03E-01	39.68E-01	40.00E-01	0.050
89.85E-01	44.67E-01	45.00E-01	0.050
88.85E-01	49.68E-01	50.00E-01	0.050
87.98E-01	54.76E-01	55.00E-01	0.050
87.23E-01	59.69E-01	60.00E-01	0.050
86.61E-01	64.64E-01	65.00E-01	0.050
85.94E-01	70.00E-01	70.00E-01	0.050
85.41E-01	74.76E-01	75.00E-01	0.050
84.90E-01	79.71E-01	80.00E-01	0.050
84.44E-01	84.93E-01	85.00E-01	0.050
84.01E-01	90.25E-01	90.00E-01	0.050
83.61E-01	94.98E-01	95.00E-01	0.050
83.25E-01	10.04E+00	10.00E+00	0.050
82.91E-01	10.46E+00	10.50E+00	0.050
82.58E-01	10.96E+00	11.00E+00	0.050
82.28E-01	11.49E+00	11.50E+00	0.050
82.01E-01	12.01E+00	12.00E+00	0.050

Title: RUO2 VS TEMP PROGRAM
Run Id. - 0236LTC.DAT
Time and Date: 11:46:50 10-16-1986 - 12:48:13 10-16-1986
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Max Volts to Plot = 10.0 Volts
Plot Title = RUO2 VS TEMP
X Axis Plot Label = Sample Temp (K)
Y Axis Plot Label = RUO2 (Volts)
Start Temperature = 002 K
Temperature Step = 0.5 K
Temperature Stop = 014 K
LR400 Range = 20000 Ohms
Temperature Dev. = 0.050 K
Wait Time = 0010 seconds
Notebook messages = 4
RUO2 Calibration vs C2329 Carbon Glass Resistor
4 WIRE CONFIGURATION FOR BOLOMETER
BACKGROUND MEASUREMENT
STEPPING UP
Number of points = 21 Values per point = 4

RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
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96.15E-01	25.17E-01	25.00E-01	0.050
94.16E-01	29.68E-01	30.00E-01	0.050
92.41E-01	34.72E-01	35.00E-01	0.050
91.03E-01	39.68E-01	40.00E-01	0.050
89.85E-01	44.67E-01	45.00E-01	0.050
88.85E-01	49.68E-01	50.00E-01	0.050
87.98E-01	54.76E-01	55.00E-01	0.050
87.23E-01	59.69E-01	60.00E-01	0.050
86.61E-01	64.64E-01	65.00E-01	0.050
85.94E-01	70.00E-01	70.00E-01	0.050
85.41E-01	74.76E-01	75.00E-01	0.050
84.90E-01	79.71E-01	80.00E-01	0.050
84.44E-01	84.93E-01	85.00E-01	0.050
84.01E-01	90.25E-01	90.00E-01	0.050
83.61E-01	94.98E-01	95.00E-01	0.050
83.25E-01	10.04E+00	10.00E+00	0.050
82.91E-01	10.46E+00	10.50E+00	0.050
82.58E-01	10.96E+00	11.00E+00	0.050
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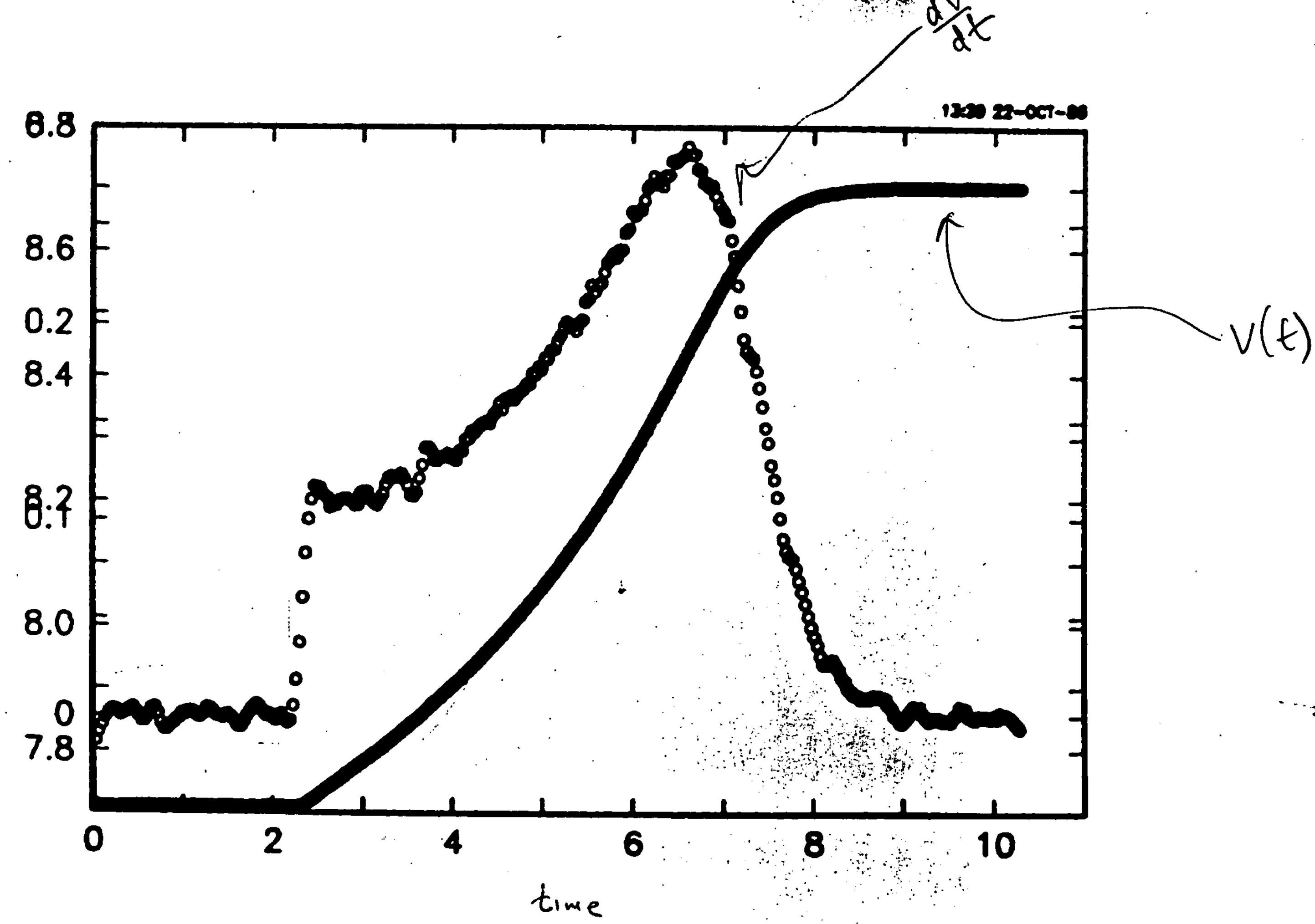
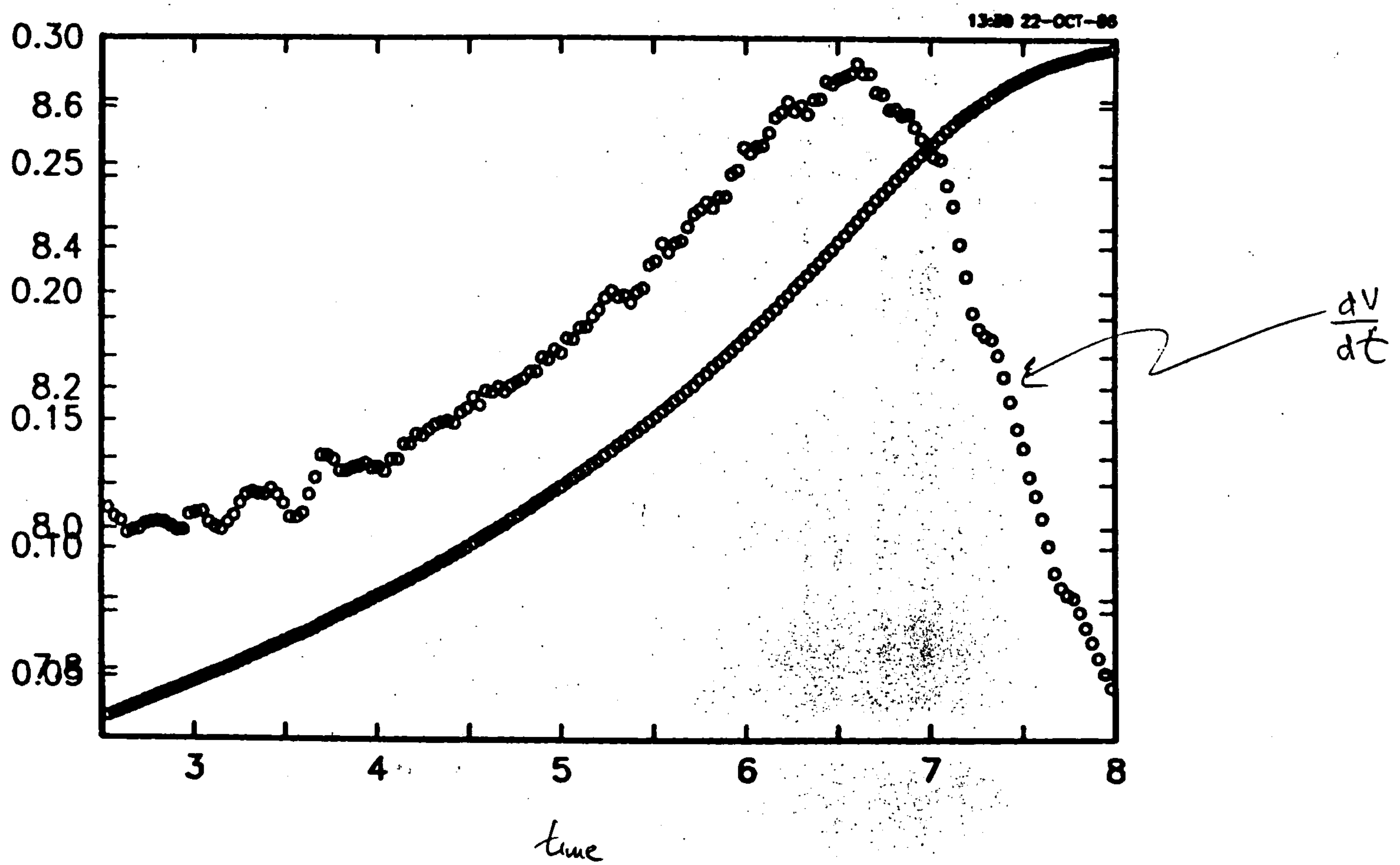
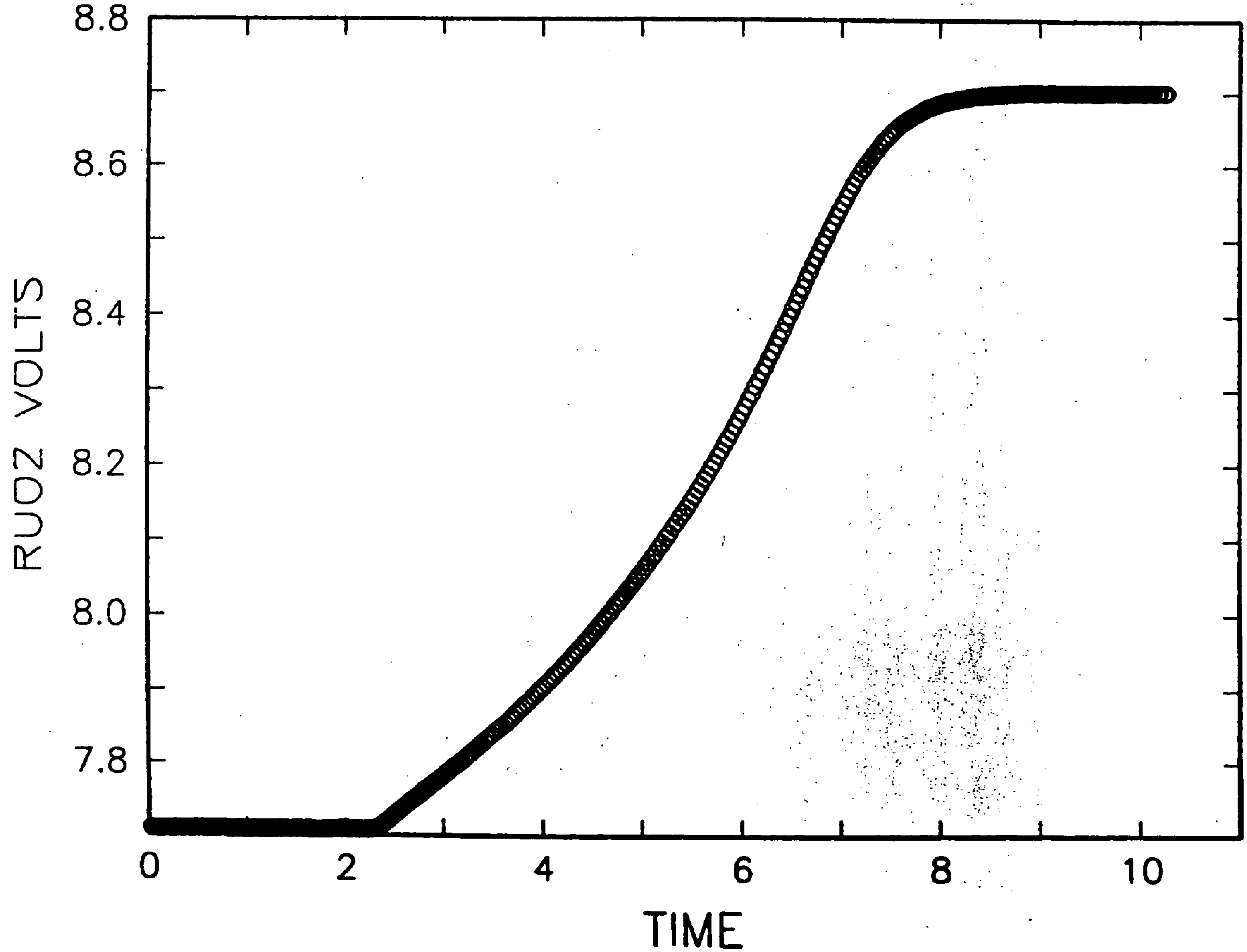


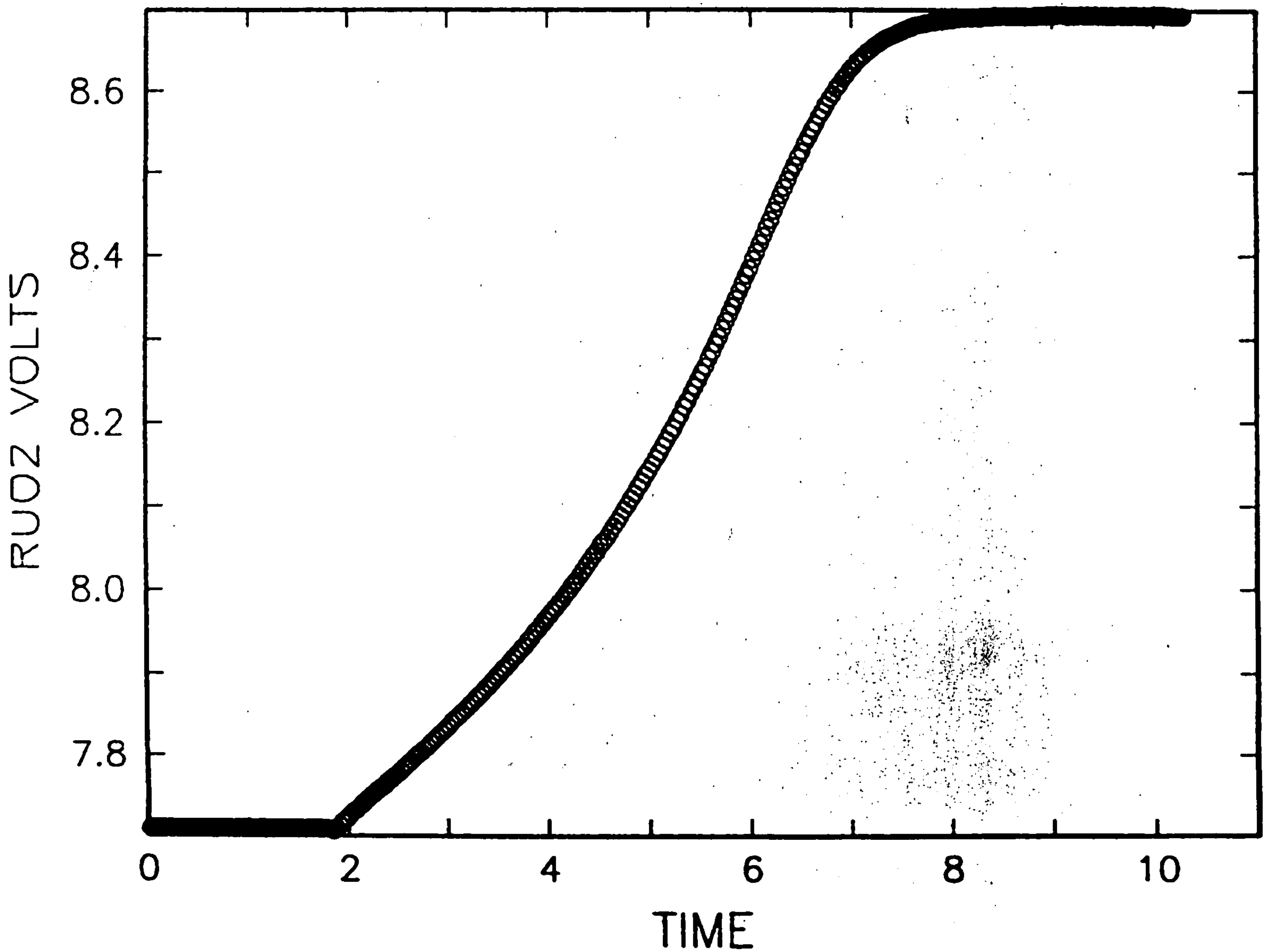
dV/dt
13:20 22-OCT-86
8.8
8.6
0.2
8.4
8.2
0.1
8.0
0
7.8
0
2
4
6
8
10
V(t)
time


13:30 22-OCT-86
0.30
8.6
0.25
8.4
0.20
8.2
0.15
8.0
0.10
7.8
0.05
3
4
5
6
7
8
time
dV/dt

Y BGHB zero suppressed

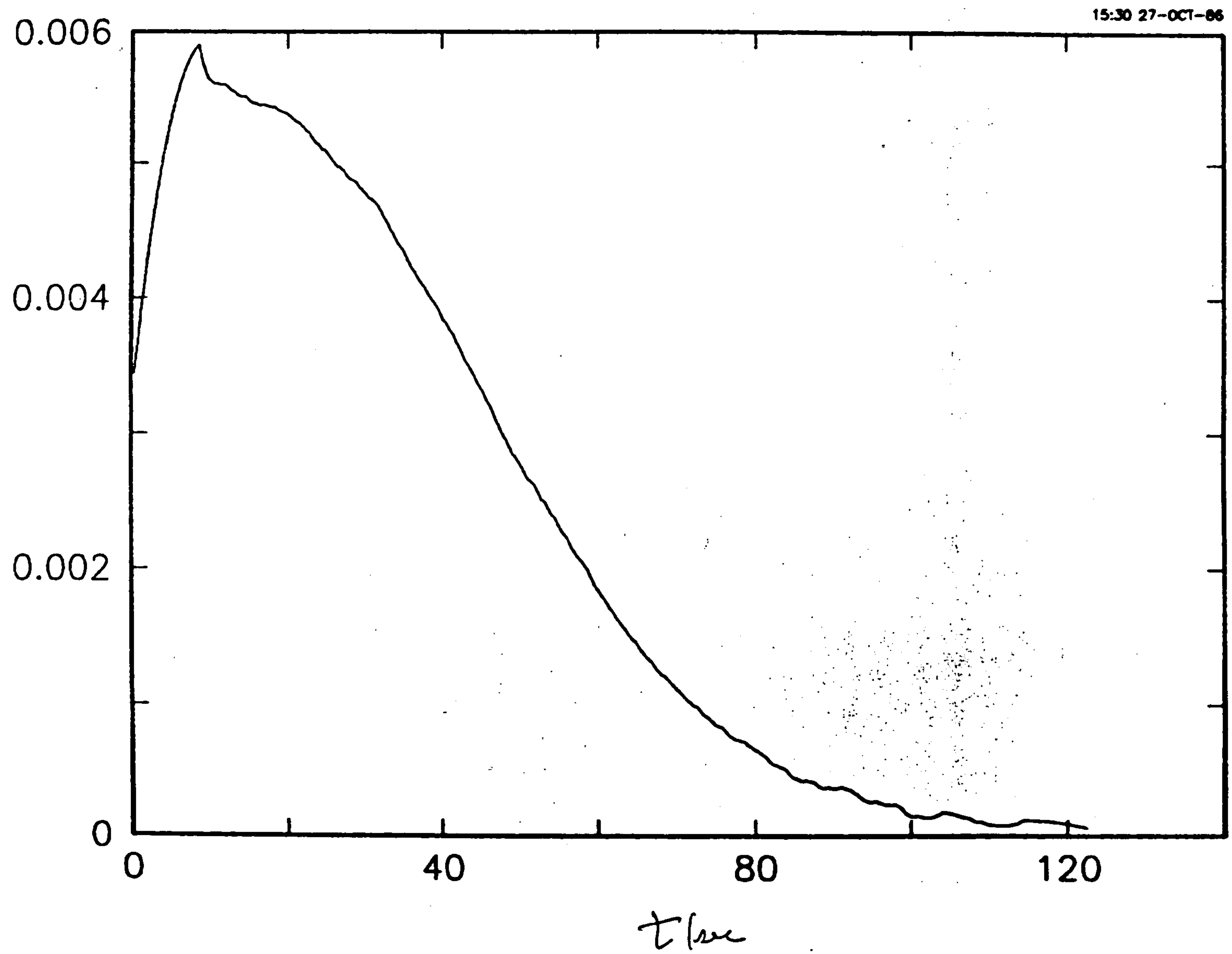


Backyrd 10/22/86 YBGH No filter
Not zero suppressed



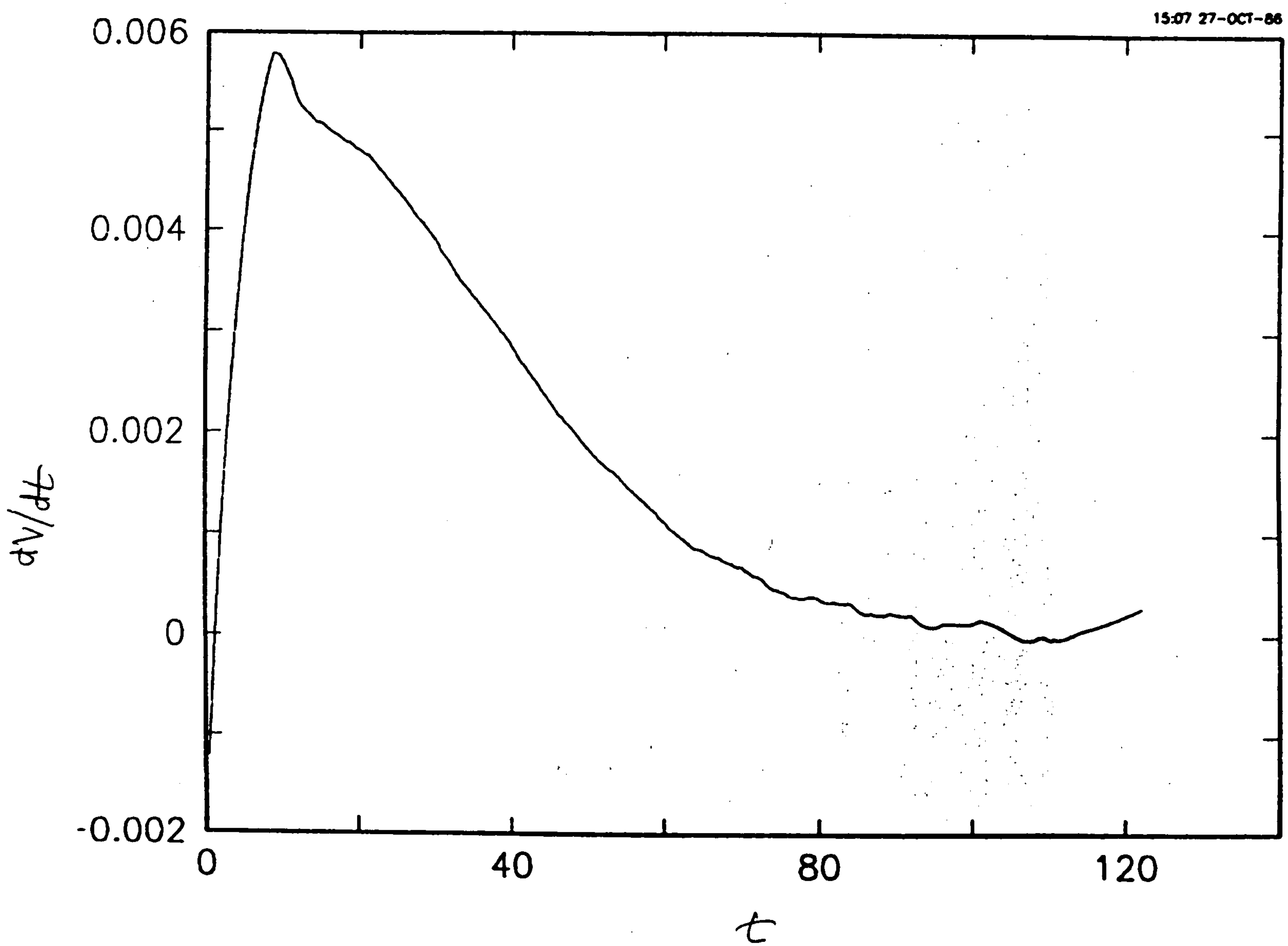
027620HB (39 to 24K)

PC fit AA = 20



6276 20 HA

PC fit AA = 20



027620HA

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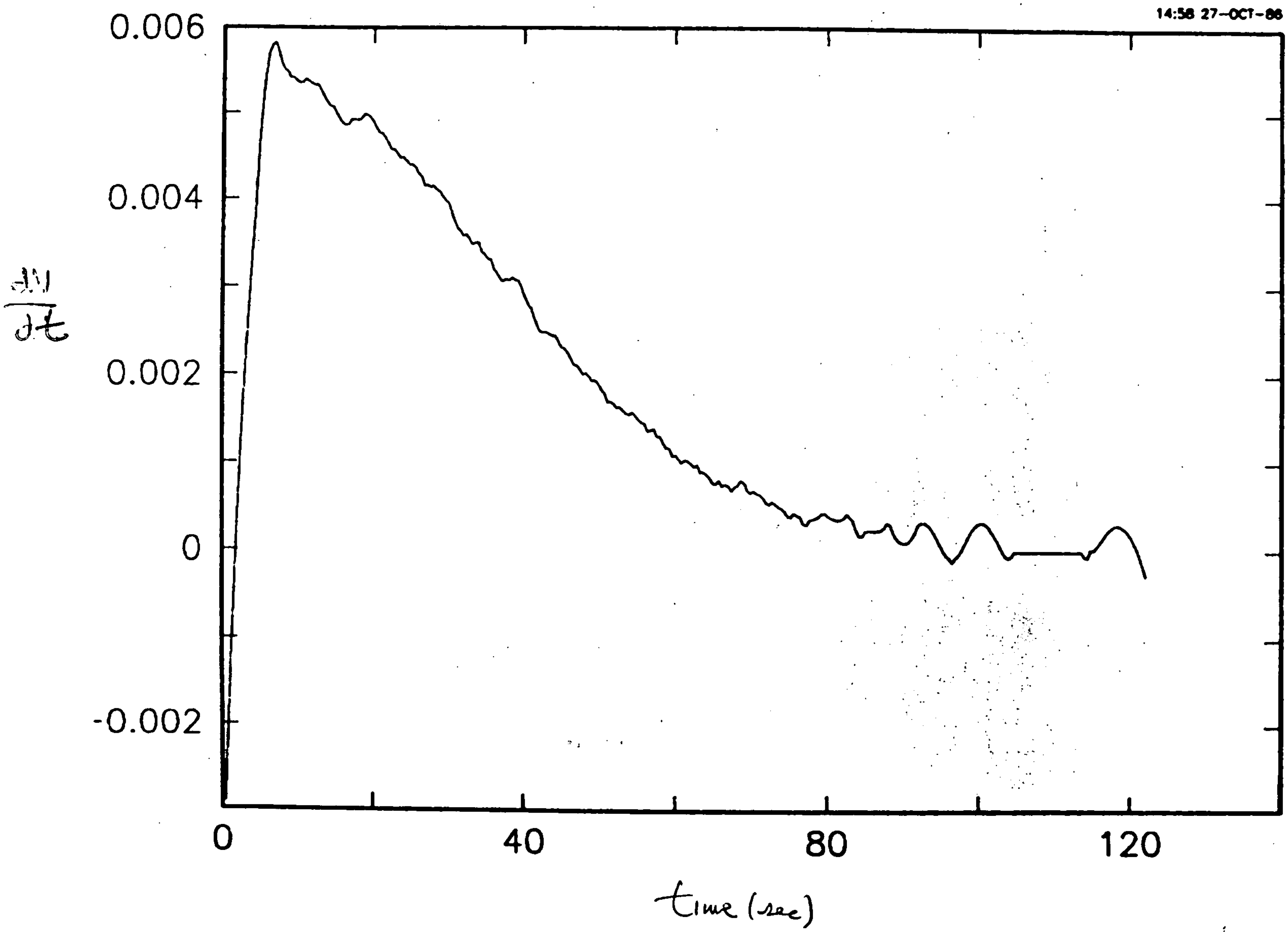
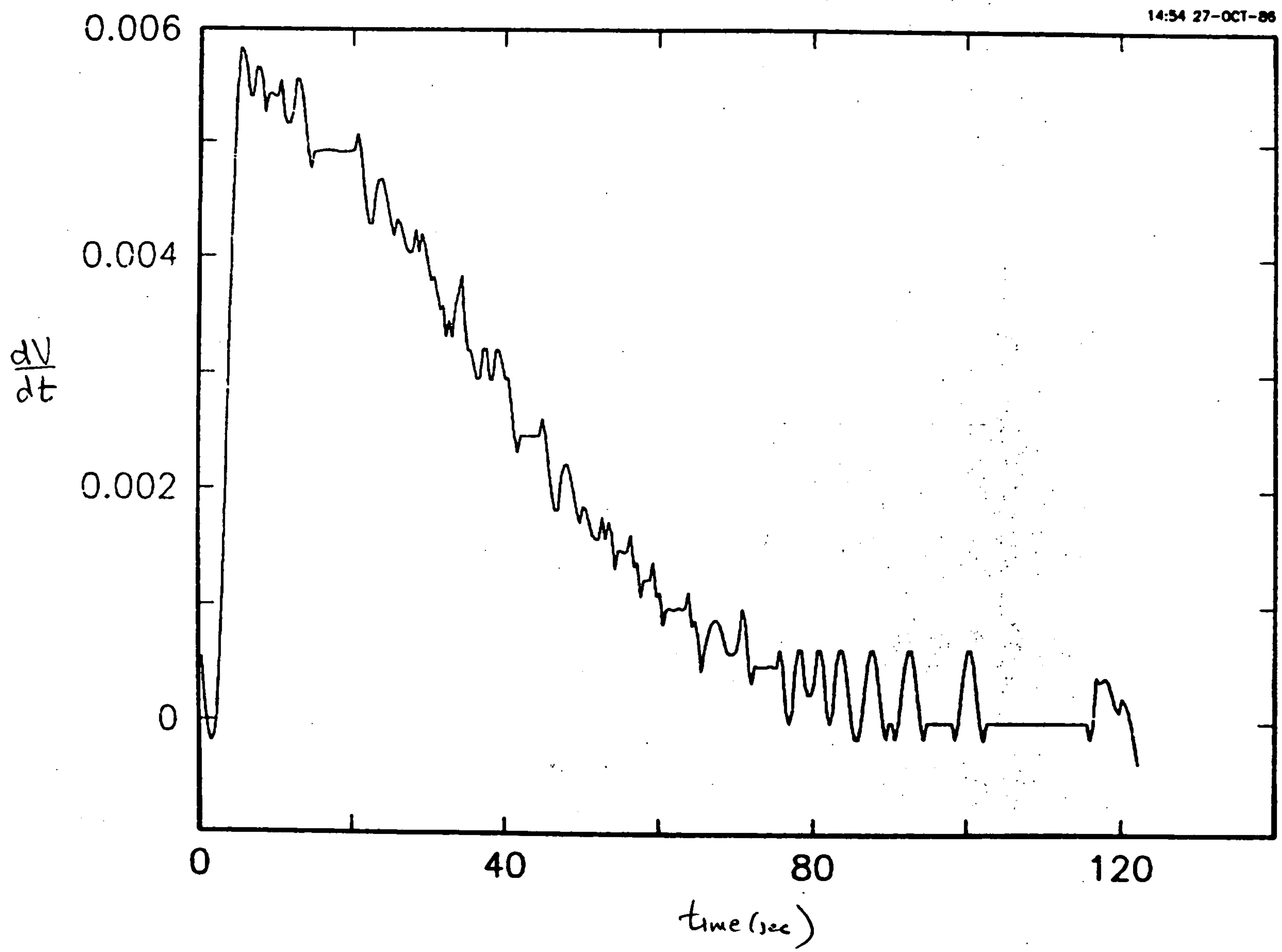
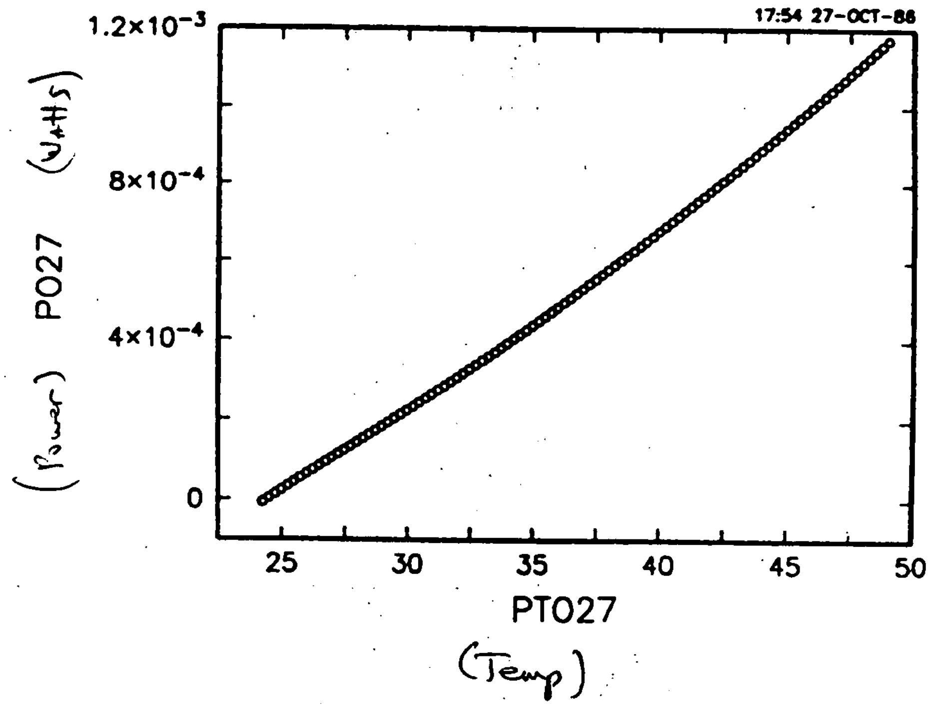


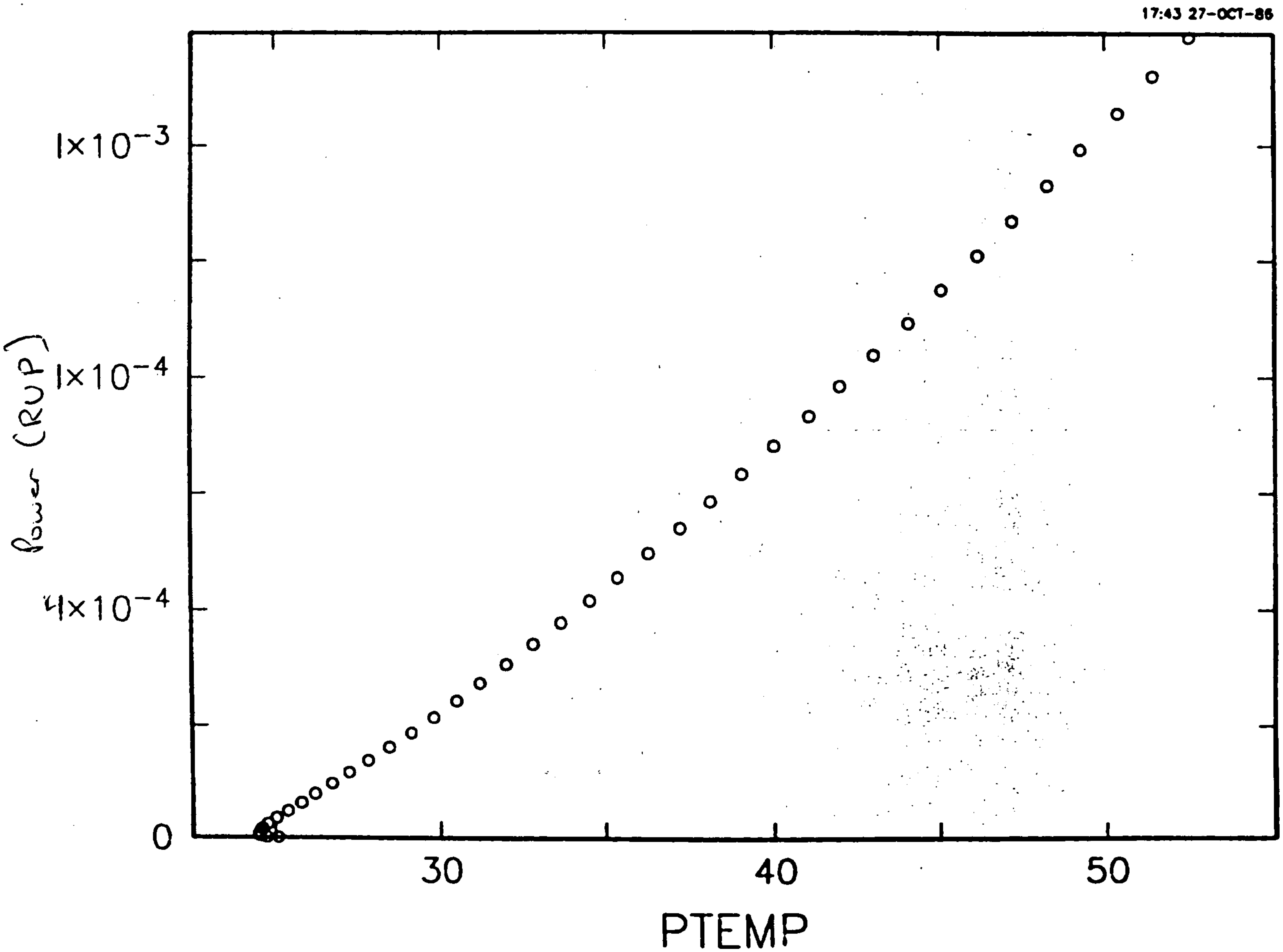
027620HA (24-35K)

PCfit AA=4



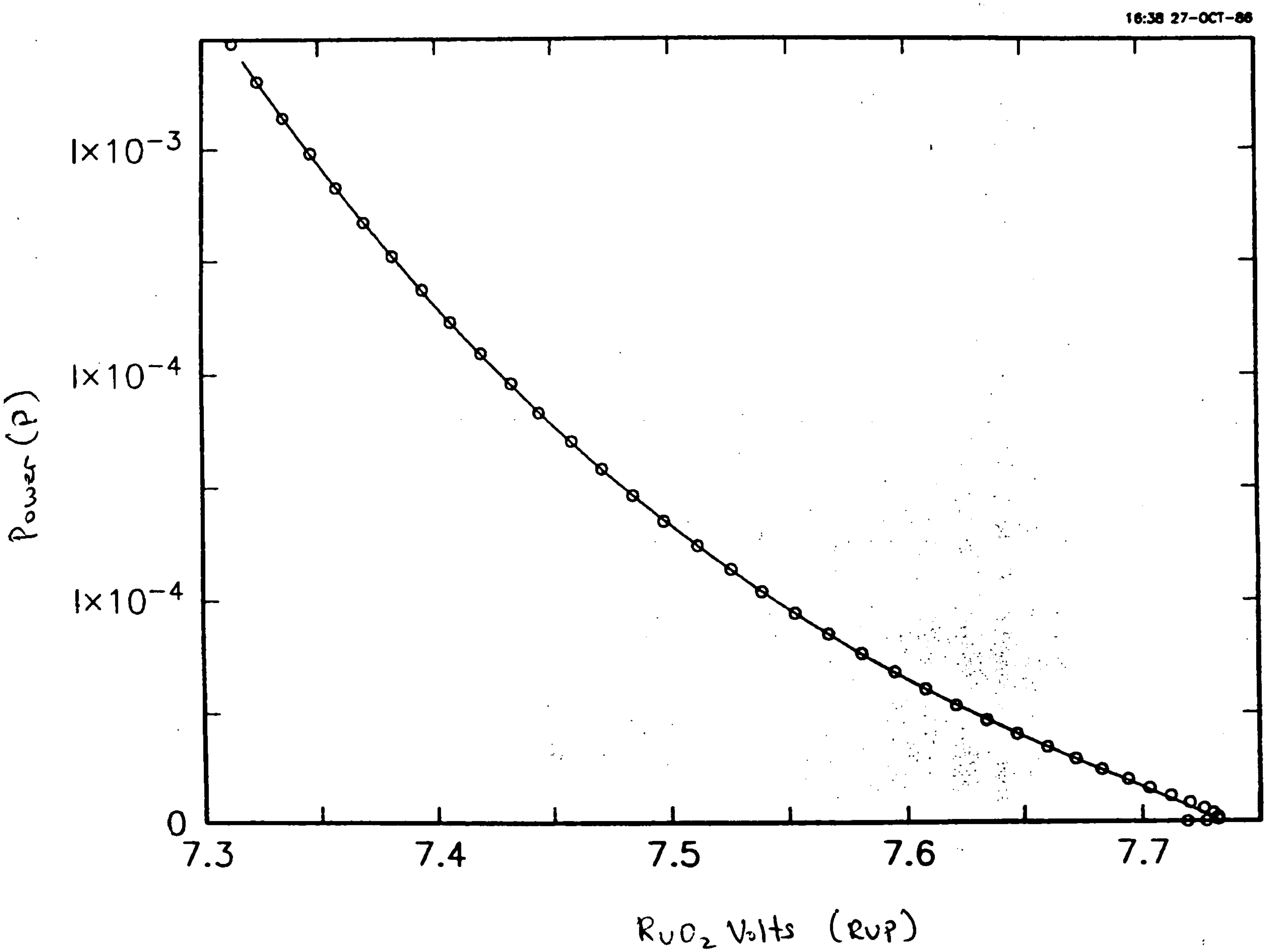
From fit of RUP vs PTemp



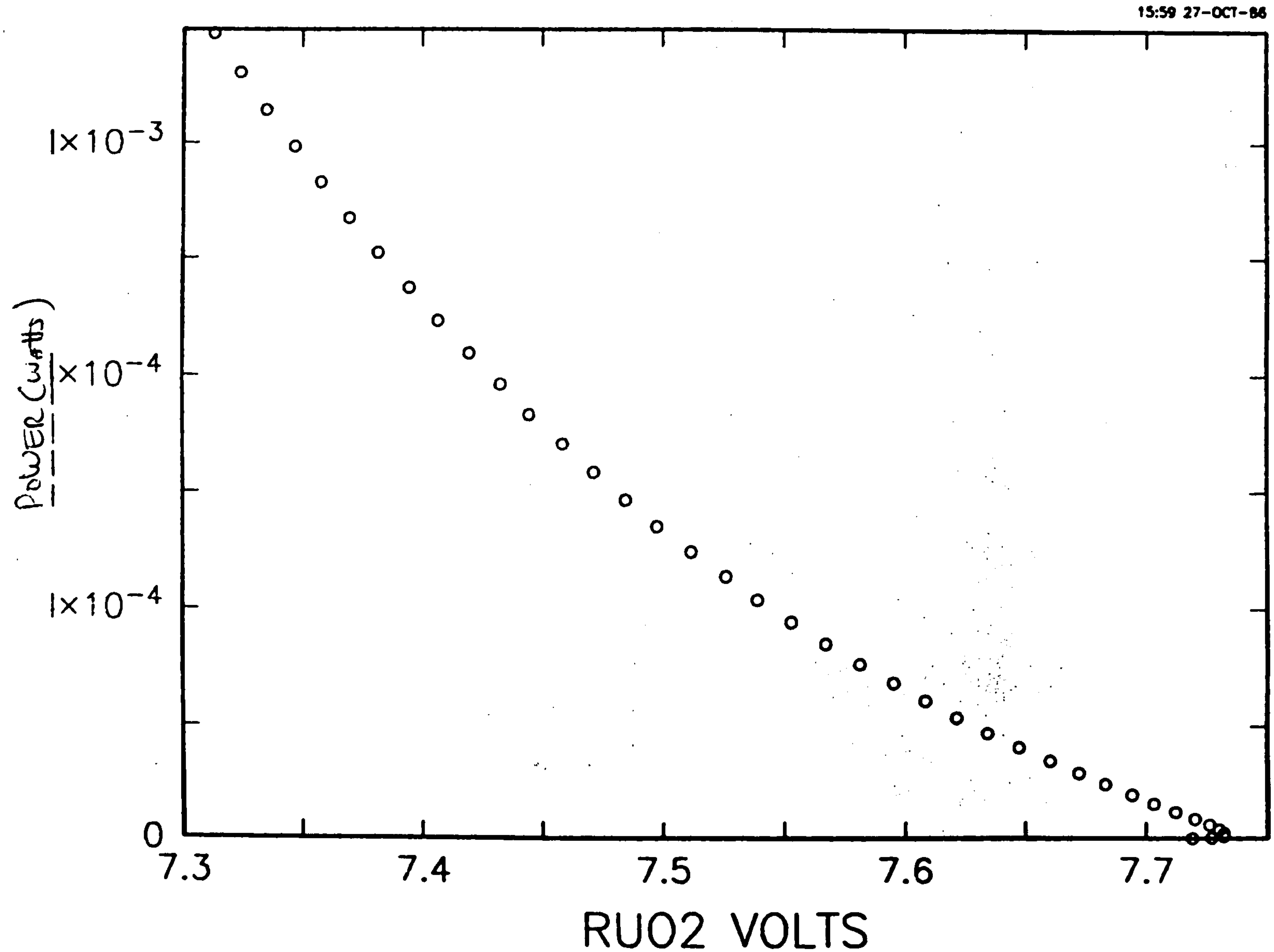


17:43 27-OCT-86
1×10−3
1×10−4
4×10−4
0
Power (RUP)
30
40
50
PTEMP

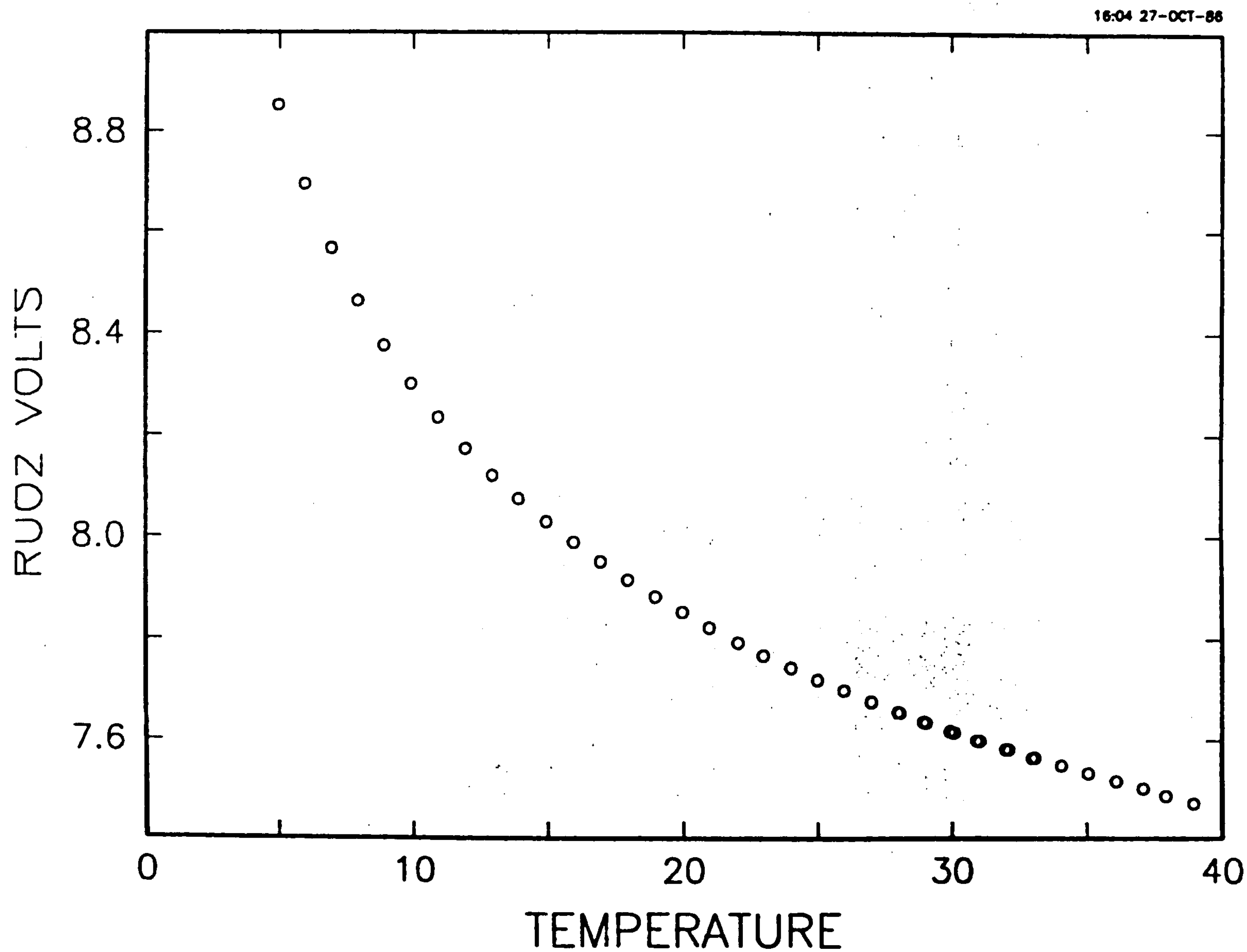
Fit to P vs Volts

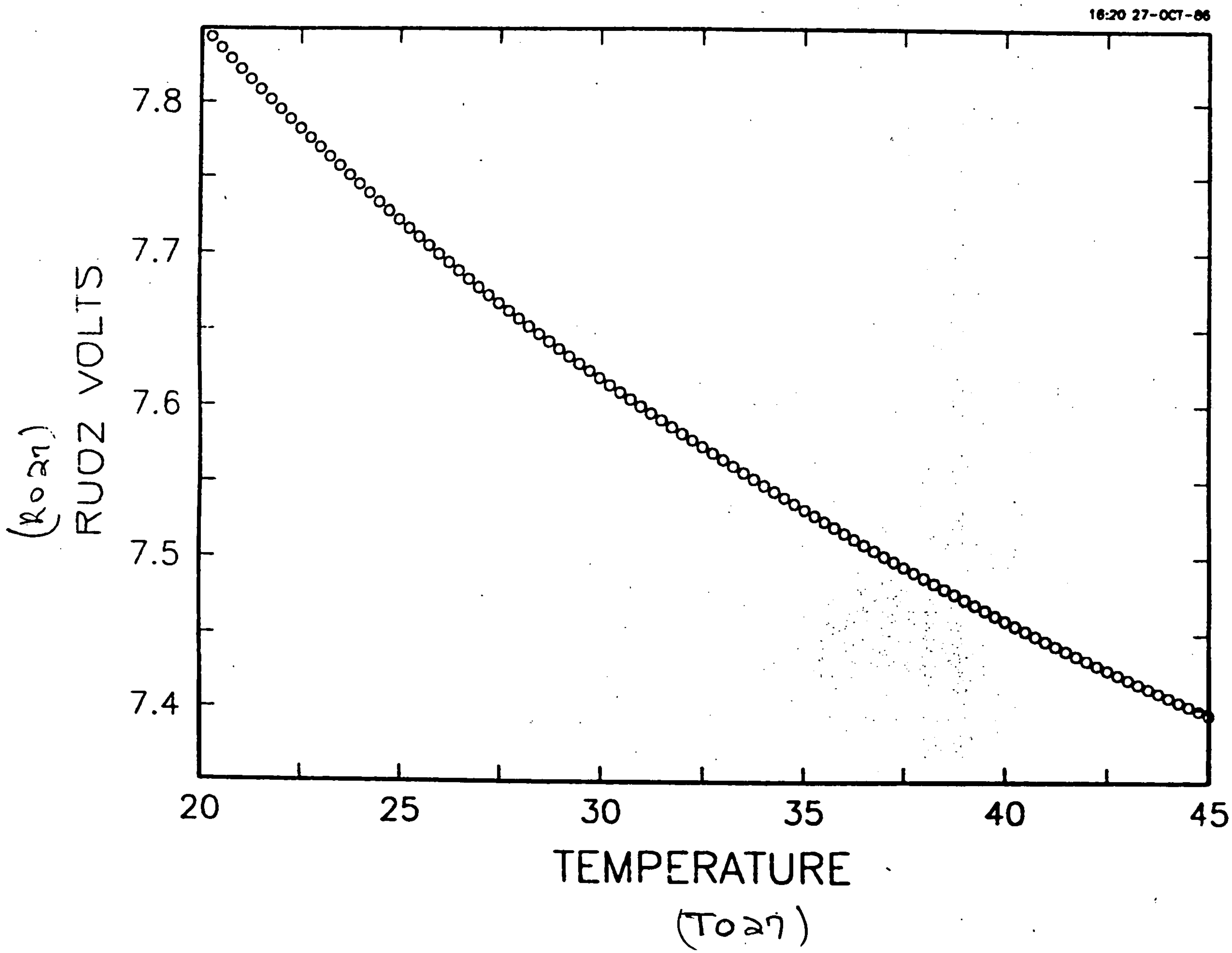


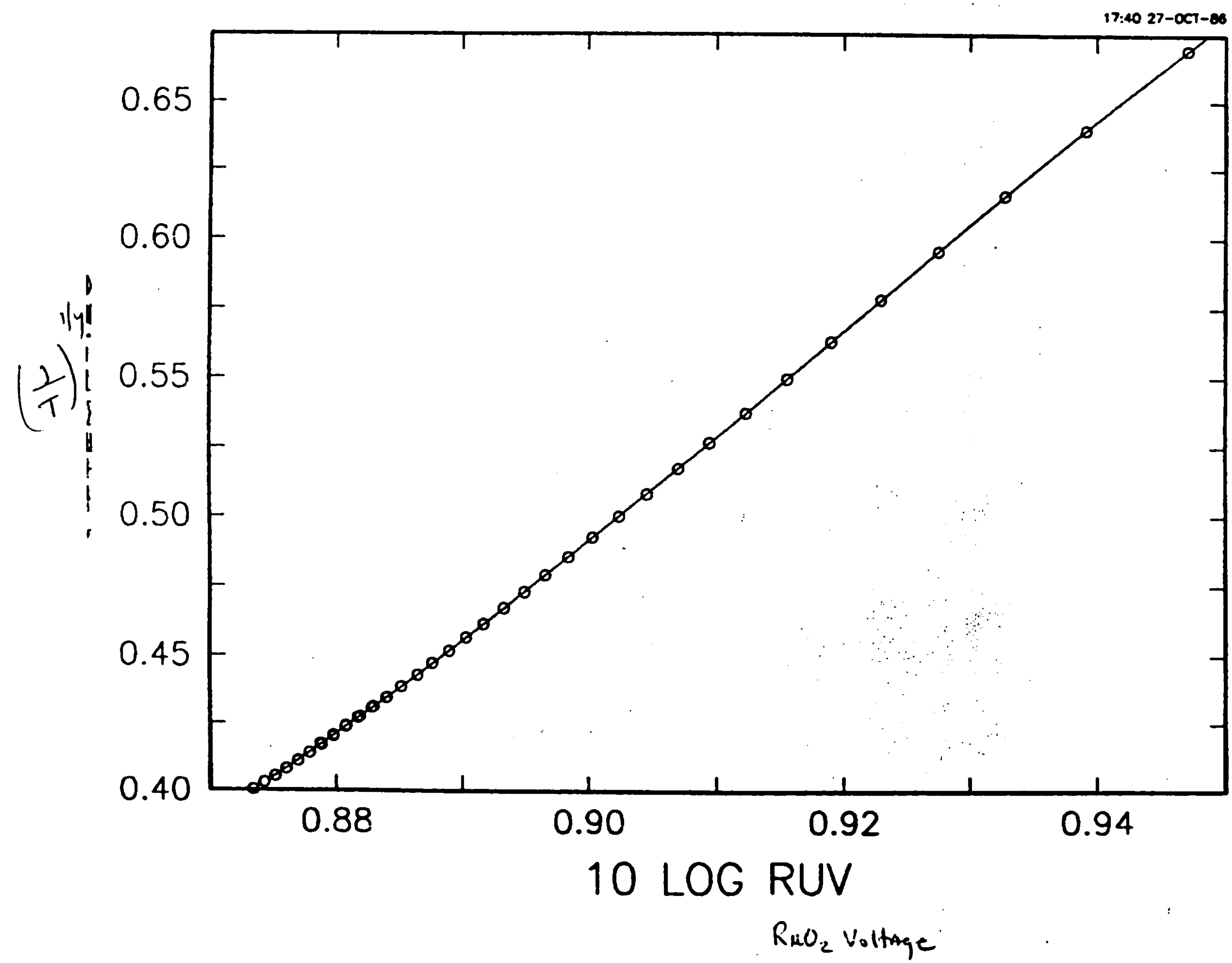
0276PCH.DAT — (24 → 50K) Power Calibration

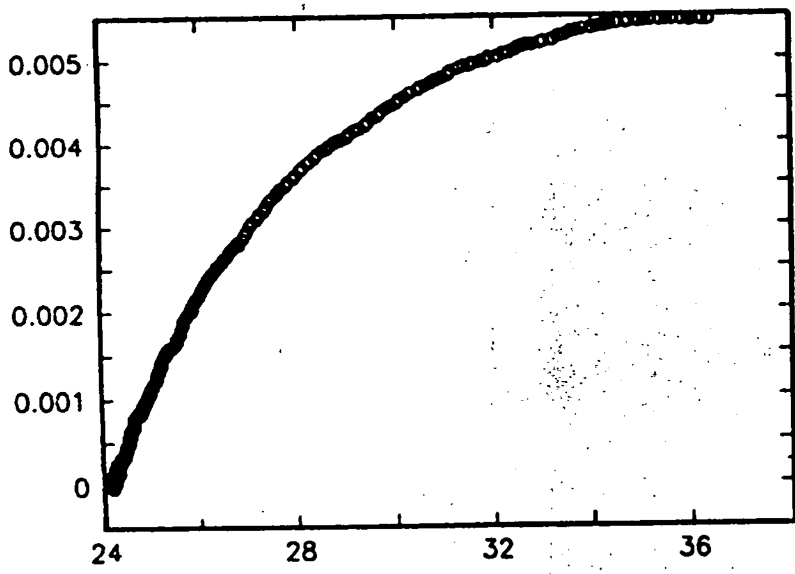


0216HTCU.DAT
0216HTCB.DAT } files for RuO_2 calibration

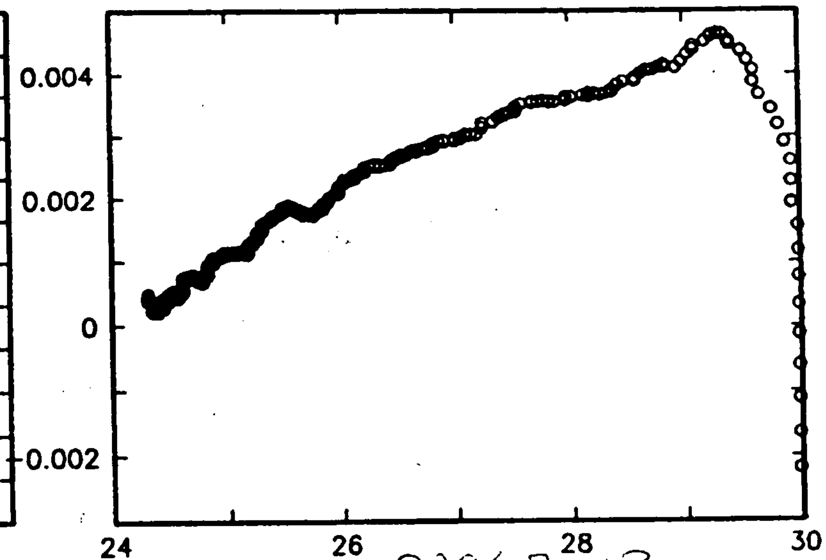



16:20 27-OCT-86
(R027)
RUO2 VOLTS
7.8
7.7
7.6
7.5
7.4
20
25
30
35
40
45
TEMPERATURE
(T027)


17:40 27-OCT-86
0.65
0.60
0.55
0.50
0.45
0.40
0.88
0.90
0.92
0.94
10 LOG RUV
$\left(\frac{1}{T}\right)^{1/4}$
RuO_2 Voltage



029620HC



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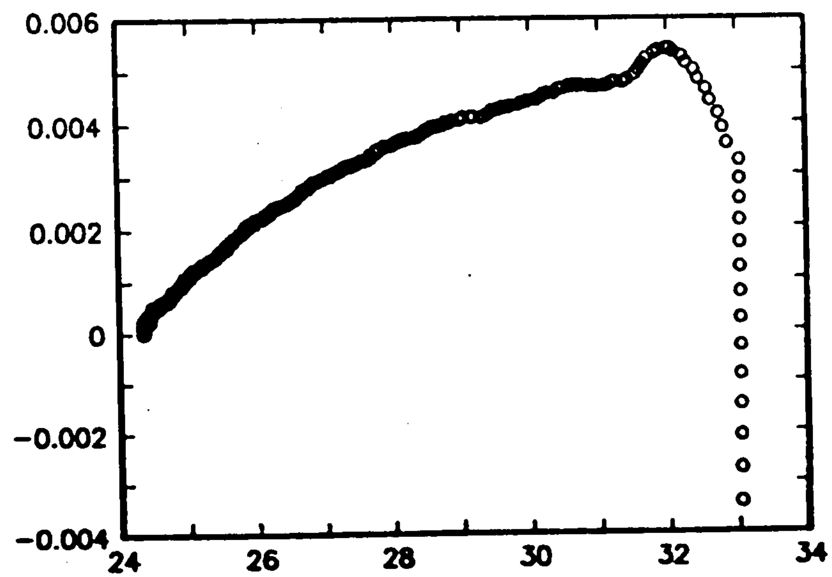
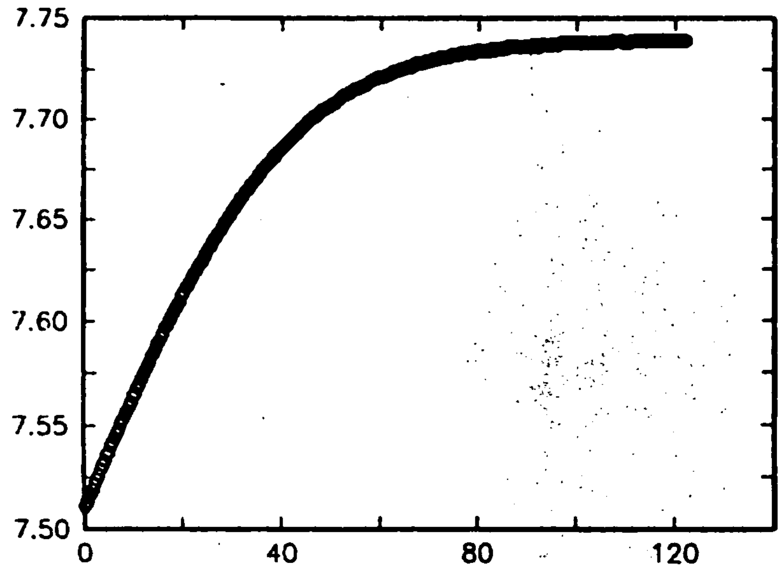
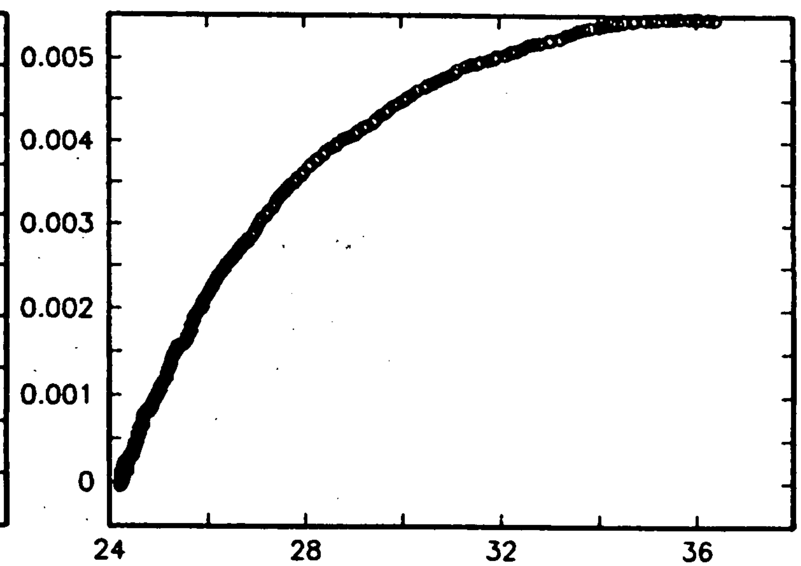


029620HA

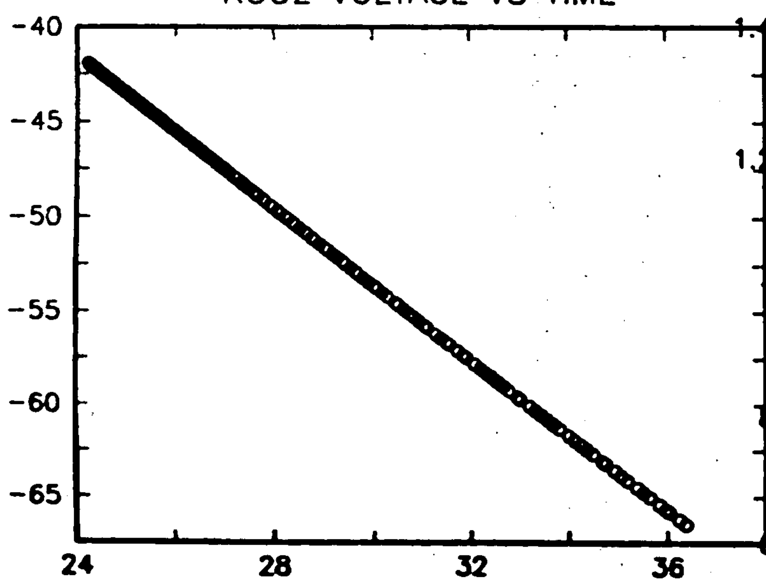
0296ZOHC



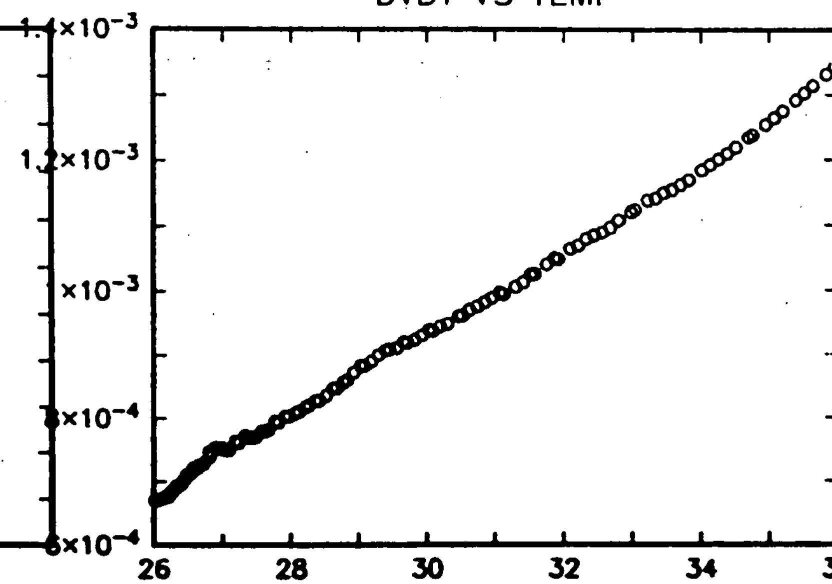
RUO2 VOLTAGE VS TIME



DVDT VS TEMP



DTDV VS TEMP



HEAT CAPACITY VS TEMP

PAR124A
100 MS

[16] A. VERBAERE and M. TOURNOUX, *Bull. Soc. Chim.*, 1973, 1237.
[17] A. D. WADSLEY, *Acta Cryst.*, 1964, 17, 623.
[18] H. REBBAH, G. DESGARDIN and B. RAVEAU, *J. Solid State Chem.*, 1980, 31, 321.
[19] M. HERVIEU, H. REBBAH, G. DESGARDIN and B. RAVEAU, *J. Solid State Chem.*, 1980, 35, 200.
[20] M. HERVIEU and B. RAVEAU, *J. Solid State Chem.*, 1980, 32, 161.
[21] H. REBBAH, J. PANNETIER and B. RAVEAU, *J. Solid State Chem.*, 1982, 41, 57.
[22] A. LECLAIRE, J. C. MONIER and B. RAVEAU, *Acta Cryst.* (to be published).
[23] C. MICHEL, C. ROBERT, D. GROULT and B. RAVEAU, *Mat. Res. Bull.*, 1975, 10, 949.

(Received November 30, 1983).

KZO

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Oxygen intercalation in mixed valence copper oxides related to the perovskites

by

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ABSTRACT. — Intercalation of oxygen in ternary copper oxides has been studied for three series of compounds: $Ba_3La_3Cu_6O_{14+\delta}$, $La_{2-x}A_{1+x}Cu_2O_{6-x/2+\delta}$ and $La_{2-x}A_xCuO_{4-x/2+\delta}$ (A = Ca, Sr, Ba). These mixed valence copper oxides, characterized by the presence of Cu(II) and Cu(III) simultanously are oxygen defect compounds whose structure is closely related to that of the perovskite, and to those of the two members of the intergrowths SrO-perovskite: $Sr_3Ti_2O_7$ and K_2NiF_4 respectively. The localization of the oxygen vacancies in (0 0 1) planes of these structures makes that two of these families: $Ba_3Ca_3Cu_6O_{14+\delta}$ and $La_{2-x}A_{1+x}Cu_2O_{6-x/2+\delta}$ can be considered in their most reduced state as oxides with low dimensionality. The influence of oxygen intercalation on the structure is described. The electrical properties of these phases are described and discussed: they are strongly influenced by the intercalation process. A progressive transition from a *p* type semi-conductive to a *p* type semi-metallic or metallic state is indeed observed which depends on the oxygen pressure and on the nature of the oxides.

RÉSUMÉ. — L'intercalation d'oxygène dans les oxydes ternaires de cuivre a été étudiée pour trois séries de composés : $Ba_3La_3Cu_6O_{14+\delta}$, $La_{2-x}A_{1+x}Cu_2O_{6-x/2+\delta}$ et $La_{2-x}A_xCuO_{4-x/2+\delta}$(A = Ca, Sr, Ba). Ces oxydes de cuivre à valence mixte, caractérisés par la présence simultanée de Cu(II) et Cu(III), sont des composés déficitaires en oxygène dont la structure est étroitement liée respectivement à celle de la pérovskite et à celles des deux membres de la série d'intercroissances pérovskite-SrO : $Sr_3Ti_2O_7$ et K_2NiF_4. La localisation des lacunes anioniques dans les plans (0 0 1) de ces structures fait que deux de ces familles : $Ba_3La_3Cu_6O_{14+\delta}$ et $La_{2-x}A_{1+x}Cu_2O_{6-x/2+\delta}$ peuvent être considérées, dans leur état le plus réduit, comme des oxydes de basse dimensionalité. L'influence de l'intercalation d'oxygène dans la structure est décrite. Les propriétés électriques de ces phases sont décrites et discutées : elles sont fortement influencées par le processus d'intercalation. Une transition progressive d'un état semi-conducteur de type *p* à un état semi-métallique ou métallique de même type, qui dépend de la pression d'oxygène et de la nature des oxydes, est en effet observée.

REVUE DE CHIMIE MINÉRALE, 0035-1032/84/04/407/19/$ 3.90/

INTRODUCTION

Intercalation of oxygen in an oxide, by a simple reversible exchange with O_2 in air or in a gaseous atmosphere can be used for different applications such as electrocatalysis, or gauges for materials with electrical properties sensitive to the oxygen content. Thus it appears that such oxides must exhibit rather large oxygen defects in their « reduced » form, and must be able to absorb oxygen from atmosphere tending towards a stoichiometric phase in their « oxidized » state. This phenomenon supposes a reversible change of the oxidation state and of the coordination number of the metallic atoms which participate to the framework of the oxide. In this respect, [illegible]er oxides are very good candidates, owing to the ability of copper to take several coordinations—octahedral, square pyramidal, square planar—and several oxidations stades: + 1, + 2, + 3. Cu(II) and Cu(III) must be especially considered owing to their possibility to take the same octahedral coordination in similar structures as shown from previous works on $La_2Cu^{II}O_4$ [1-2] and $LaSrCu^{III}O_4$ [3], which are isostructural with K_2NiF_4. Ternary oxides $AxCuyO_3$ containing Cu(III) are more difficult to prepare than those with Cu(II), since oxygen pressures ranging from 1 bar [4-7] to several kbars [3-8] are most of the time necessary to synthesize these compounds. However, the presence of A elements like barium favours the formation of Cu(III) in normal pressure conditions [9-10]. The present paper deals with the soft intercalation of oxygen, *i. e.* at low pressure ($p \leqslant 1$ atm) and at low temperature ($T \sim 400$-$500°$ C) in three series of ternary copper oxides related to the perovskite [11-13] and belonging to the systems La_2O_3-AO-CuO with A = Ca, Sr, Ba. The influence of oxygen intercalation on the ele[illegible] transport properties of these phases are discussed.

STRUCTURAL CONSIDERATIONS

Three families with an oxygen defect structure have been isolated in the systems La_2O_3-AO-CuO:

— The oxygen defect perovskites $La_3Ba_3Cu_6O_{14+\delta}$.
— The oxygen defect intergrowths $Sr_3Ti_2O_7$ type,

$La_{2-x}A_{1+x}Cu_2O_{6-x/2+\delta}$ A = Ca, Sr.

— The oxygen defect intergrowth K_2NiF_4 type, $La_{2-x}A_xCuO_{4-x/2+\delta}$.

The most reduced form which has been isolated for the defect perovskites $La_3Ba_3Cu_6O_{14+\delta}$ corresponds to the formulation $La_3Ba_3Cu_6O_{14}$. Its

structure (fig. 1) can be described as an ordered oxygen defect perovskite. All the metallic sites corresponding to the stoichiometric perovskite are occupied by copper ions and lanthanum and barium ions respectively, whereas only 7/9 of the anionic sites are occupied in an ordered manner.

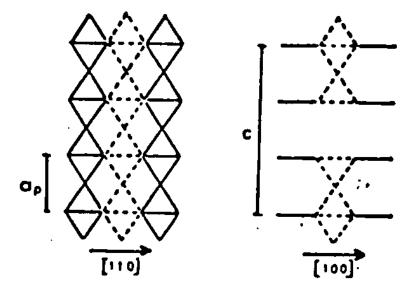


Fig. 1. — Schematic structure of a stoichiometric ABO_3 perovskite and the defect oxygen perovskite $Ba_3La_3Cu_6O_{14}$.

Considering the tetragonal cell of this compound ($a \simeq a_p\sqrt{2} = 5.525$ Å, $c \simeq 3a_p = 11.721$ Å), it can indeed be seen that the basal planes of the octahedra, parallel to (0 0 1) are preserved, that one apex out of two is missing at the levels $z = 1/6$ and $5/6$, whereas all the apices of these octahedra are missing at $z = 1/2$. It results that this reduced form can be considered as a true layer structure: double defect perovskite layers $|Ba_{1.5}La_{0.5}Cu_3O_7|_2$ built up from corner-sharing, octahedra CuO_6 square pyramids CuO_5 and square groups CuO_4 are observed whose cohesion is ensured by lanthanum ions located at $z = 1/2$. It is remarkable that such an oxide is characterized by a high Cu(III) content in spite of the high oxygen defect content. Site potential calculations confirm that the Cu^{3+} ions are located preferentially on the octahedral sites. It must also be noted that this limit compound has not really been synthesized. By heating in air at 1 000° C for 24 h the mixture of La_2O_3, CuO and $BaCO_3$ and quenching the samples at room-temperature a slight excess of oxygen is indeed observed corresponding to the formulation $La_3Ba_3Cu_6O_{14.10}$. The most reduced phase $La_3Ba_3Cu_6O_{14.05}$ is then synthesized by annealing the sample $La_3Ba_3Cu_6O_{14.10}$ at 400° C under low oxygen pressure ($\sim 5.10^{-3}$ bar) during several hours.

The deviation from stoichiometry in the oxides $La_{2-x}A_{1+x}Cu_2O_{6-x/2+\delta}$ is more complex owing to the possibility of substitution of calcium or strontium for lanthanum, in a small homogeneity range ($0 \leqslant x \leqslant 0.14$ for

strontium and $x = 0.10$ for calcium). The most reduced oxide which has been isolated in this family corresponds to the formulation $La_2SrCu_2O_6$. Its tetragonal cell ($a = 3.865$ Å, $c = 19.887$ Å), corresponds to a structure closely related to that of $Sr_3Ti_2O_7$ (fig. 2 *a*). Cu^{2+} ions are indeed located on the Ti^{4+} sites. La^{3+} and Sr^{2+} ions are located on the Sr^{2+} sites, whereas six anionic sites out of seven are occupied by oxygen in an ordered manner; thus, this oxide can be considered as an intergrowth of double oxygen perovskite layers and SrO type layers. The perovskite layers exhibit some similarity with those observed for $La_3Ba_3Cu_6O_{14}$: the basal planes of the octahedra parallel to (0 0 1) are also preserved whereas at $z = 0$ and $z = 1/2$ all the apices of the oxygen octahedra are missing. However, the resulting configuration of the framework is different from $La_3Ba_3Cu_6O_{14}$: Cu(II) exhibits here only one coordination which is square pyramidal. Nevertheless this oxide, like $La_3Ba_3Cu_6O_{14}$, must be considered as a structure with low dimensionality. It can indeed be described as built up from slabs $|LaSrCu_2O_6|_\infty$ parallel to (0 0 1) whose cohesion is ensured by Sr^{2+} and La^{3+} ions located at $z = 0$ and $z = 1/2$. The $|LaSrCu_2O_6|_\infty$ slabs are themselves an intergrowth of SrO-type layers and corner-sharing square pyramid layers. Such slabs are in fact derived from the K_2NiF_4 structure: the latter corresponds indeed to the superposition of two $|K_2Ni_2F_6|_\infty$ slabs which would share the face of their square pyramids, forming NiF_6 octahedra (fig. 2 *b*). Like $La_3Ba_3Cu_6O_{14+\delta}$, $La_2SrCu_2O_6$ is characterized by a great stability in spite of its oxygen defect structure: it is indeed synthesized by heating the stoichiometric mixture of CuO, La_2O_3 and $SrCO_3$ at 1 050-1 100° for 24 h in air and by quenching them at room temperature in order to avoid their oxidation at lower temperature. Contrary to $La_3Ba_3Cu_6O_{14}$, copper is in its lower oxidation state, Cu(II) in this oxide.

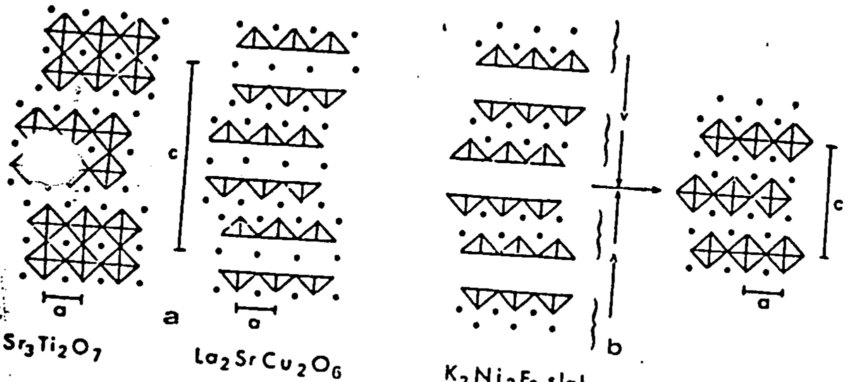


Fig. 2.

a) Schematic structure of $Sr_3Ti_2O_7$ and $La_2SrCu_2O_6$ (projection on to (1 0 0) plane), showing the oxygen vacancies.

b) Schematic representation of $K_2Ni_2F_6$ slabs sharing the square faces of the NiF_5 pyramids to give the K_2NiF_4 structure.

The oxides $La_{2-x}A_xCuO_{4-x/2+\delta}$ exhibit an oxygen defect K_2NiF_4 type structure involving different coordinations of copper: octahedral, square pyramidal and eventually square planar (fig. 3). Their oxygen content depends on the nature of the A ions (A = Ca, Sr, Ba) and on the substitution rate x which can lead to wide homogeneity ranges: $0 \leqslant x \leqslant 0.20$ for A = Ca and Ba and $0 \leqslant x \leqslant 4/3$ for A = Sr. The most reduced phase which exhibits the highest deviation from stoichiometry has been synthesized in the case of strontium for $x = 4/3$: $La_{2/3}Sr_{4/3}CuO_{3.33}$. Contrary to the two other series, the oxygen vacancies are located in the basal plane of the octahedra which are parallel to the (0 0 1) plane of the tetragonal cell ($a = 3.759$ Å, $c = 12.907$ Å). It must also be emphasized that this type of localization of the oxygen vacancies is always observed whatever the nature of the A ions, and whatever the rate of substitution x may be. However, symmetry changes and order-disorder phenomena in this plane may appear according to the nature of A and x value (table I). So, the calcium and barium oxides are characterized by a monoclinic distortion of the tetragonal K_2NiF_4 structure, whatever the x value may be $0 \leqslant x \leqslant 0.20$; the same

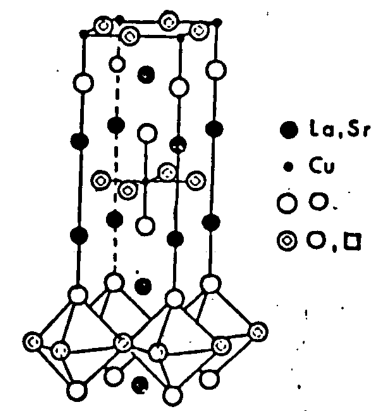
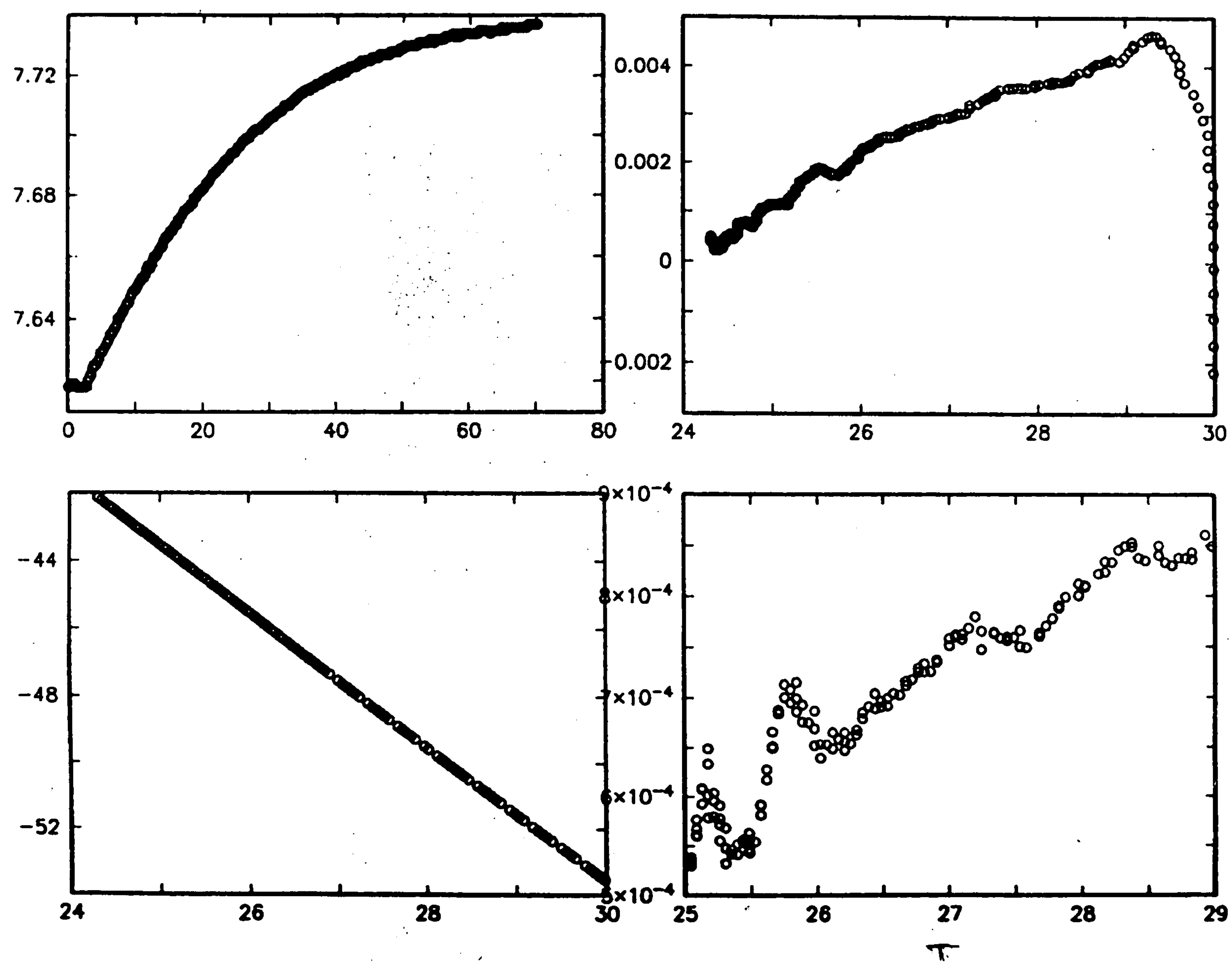


Fig. 3. — Perspective view of the structure of the oxides $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ with oxygen vacancies located in the basal plane of the octahedra.

024620HA



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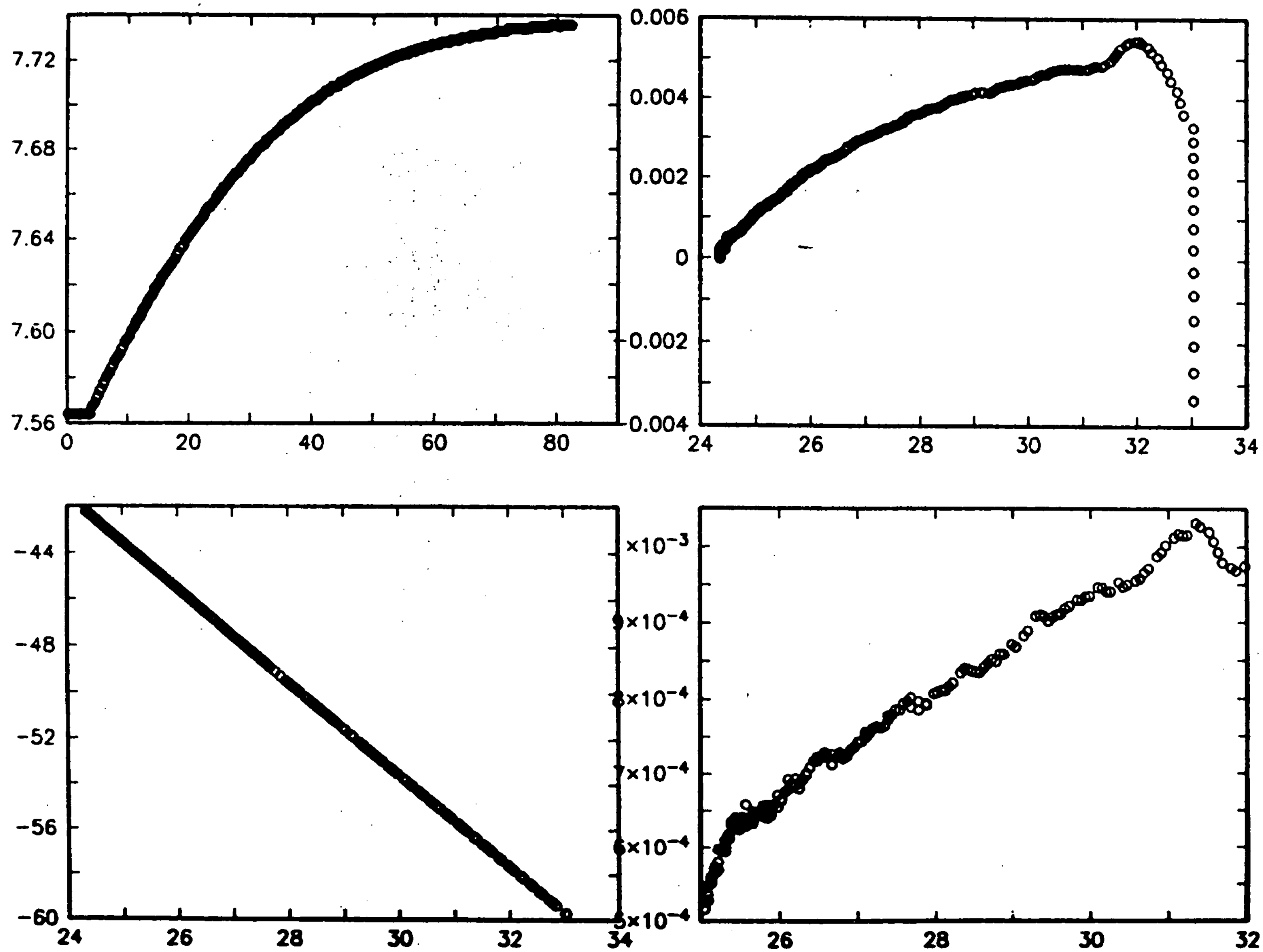
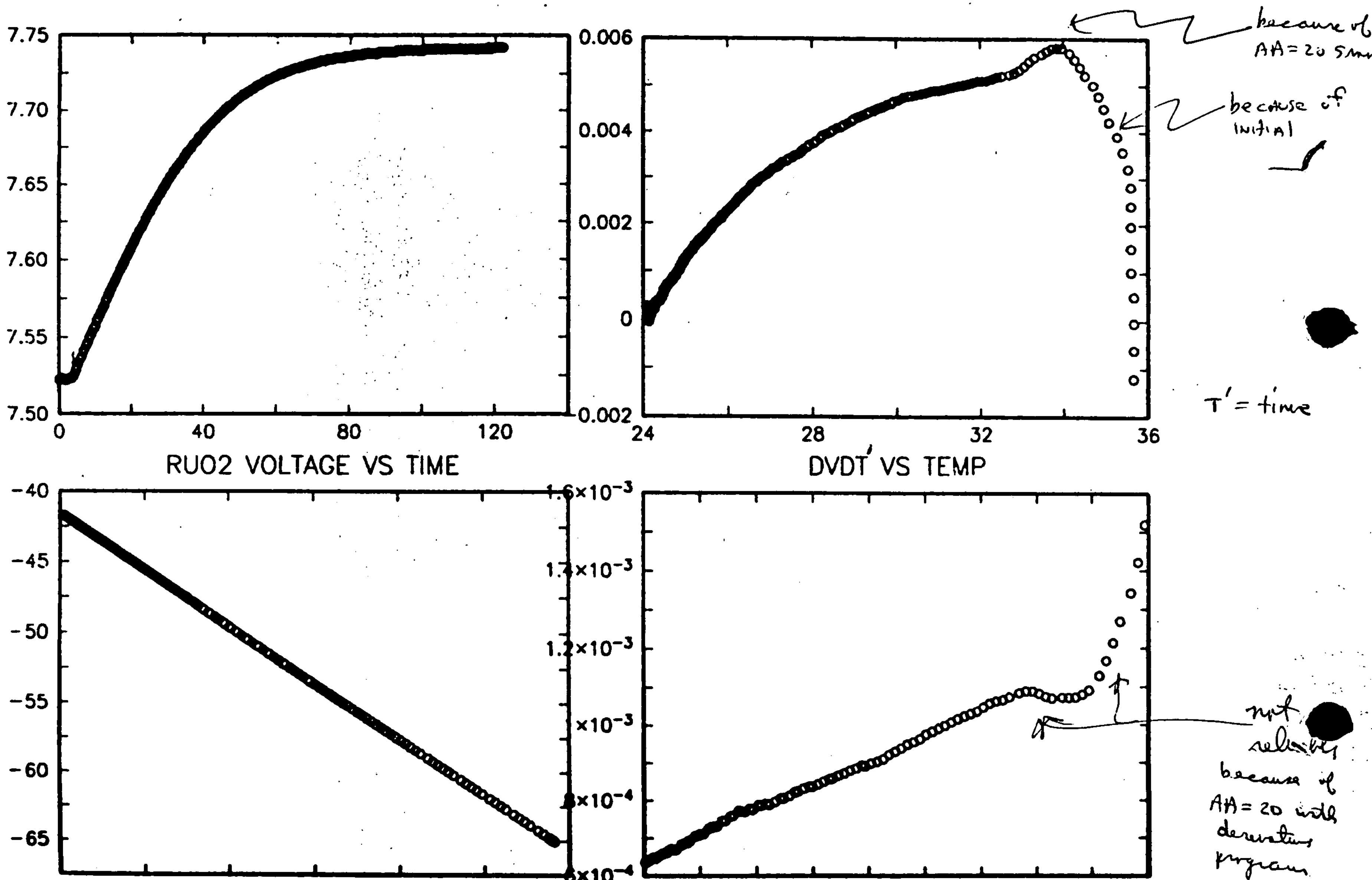


PAR124A
100 MS

O27?ZOHA

FN I



RUO2 VOLTAGE VS TIME

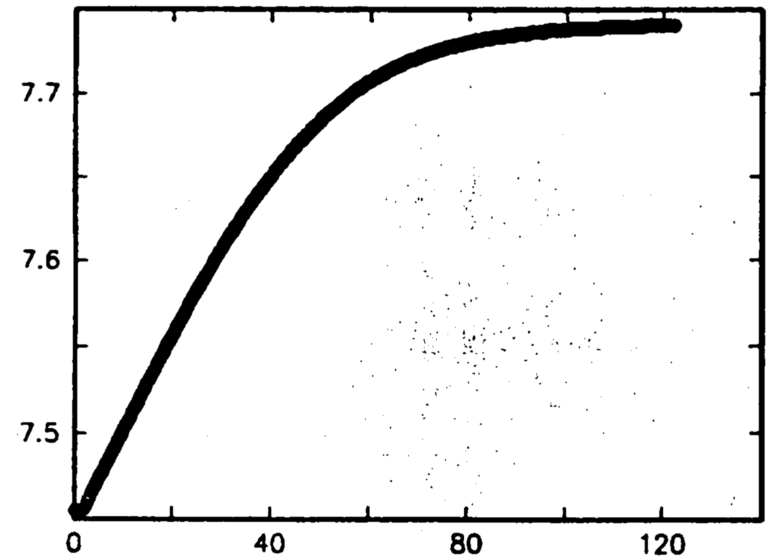
DVDT′ VS TEMP

$T' = \text{time}$

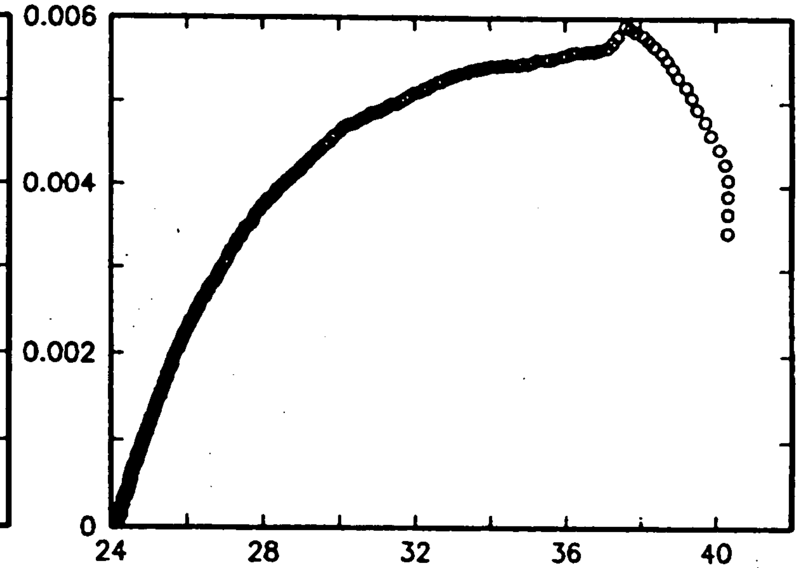
DTDV VS TEMP

HEAT CAPACITY VS TEMP

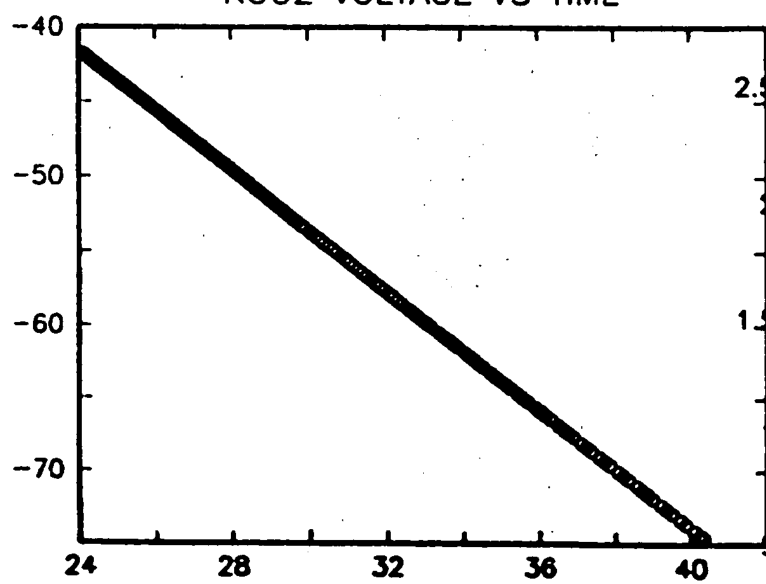
0216ZOHB
027



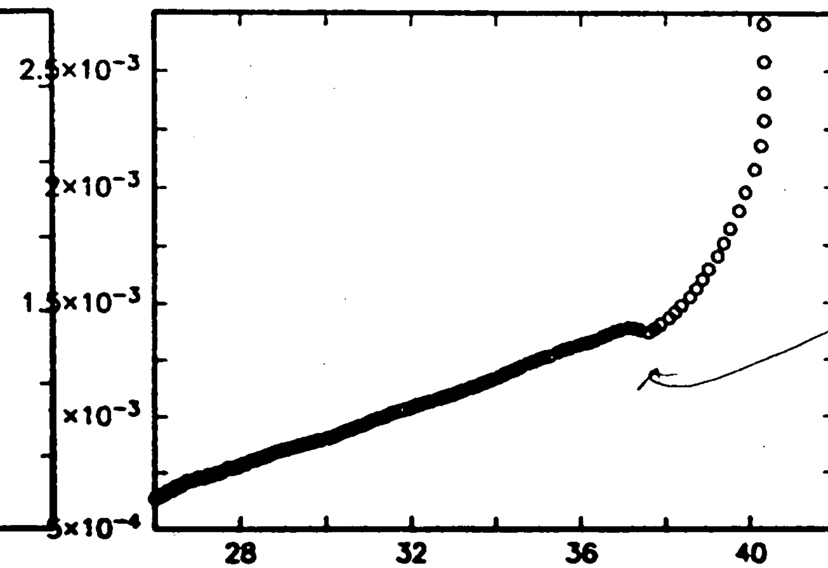
RUO2 VOLTAGE VS TIME



DVDT VS TEMP

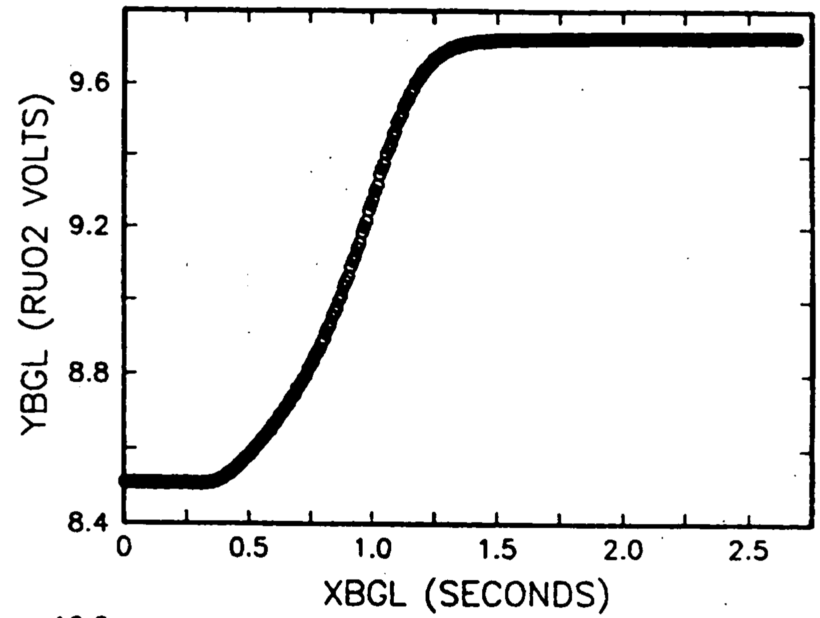


DTDV VS TEMP

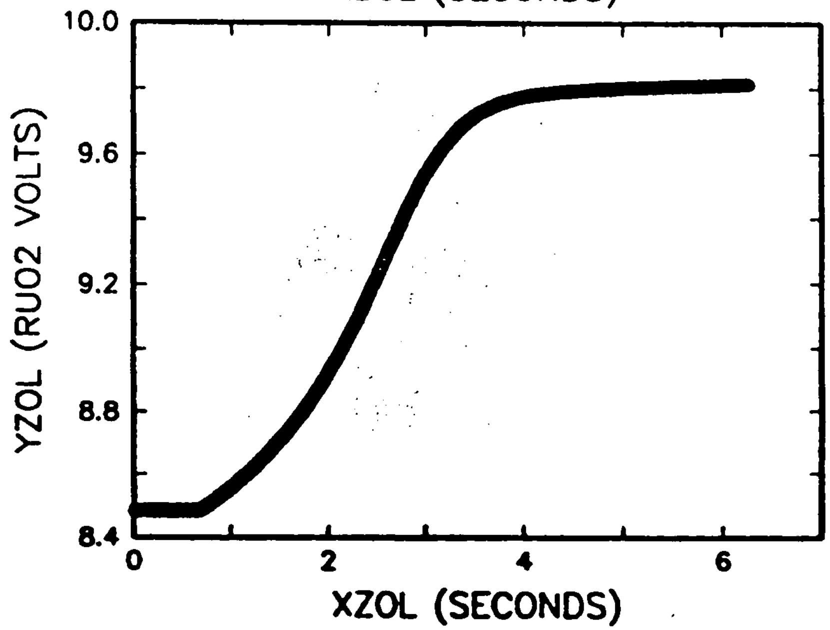


HEAT CAPACITY VS TEMP

$$C = \frac{P}{\frac{dV}{dt} \cdot \frac{dT}{dV}}$$

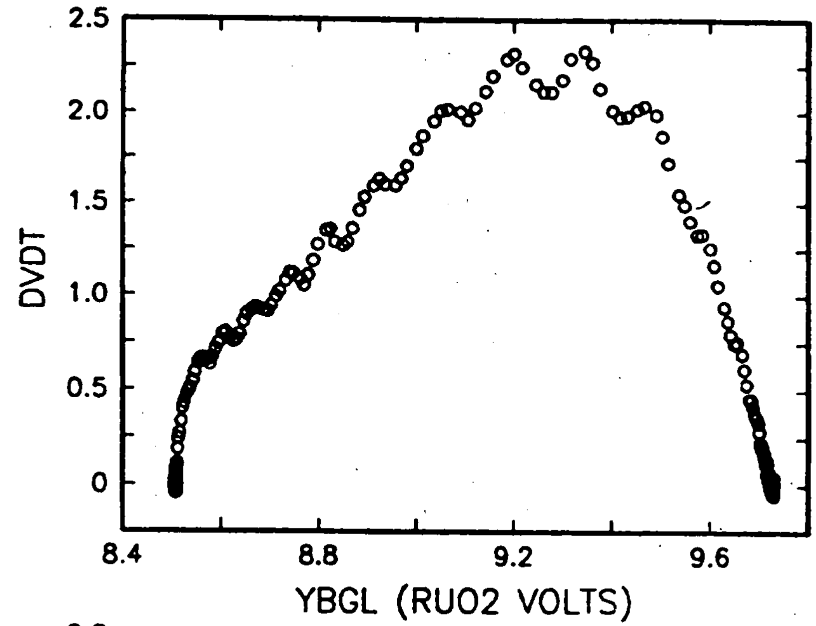


0236BGL.TXT

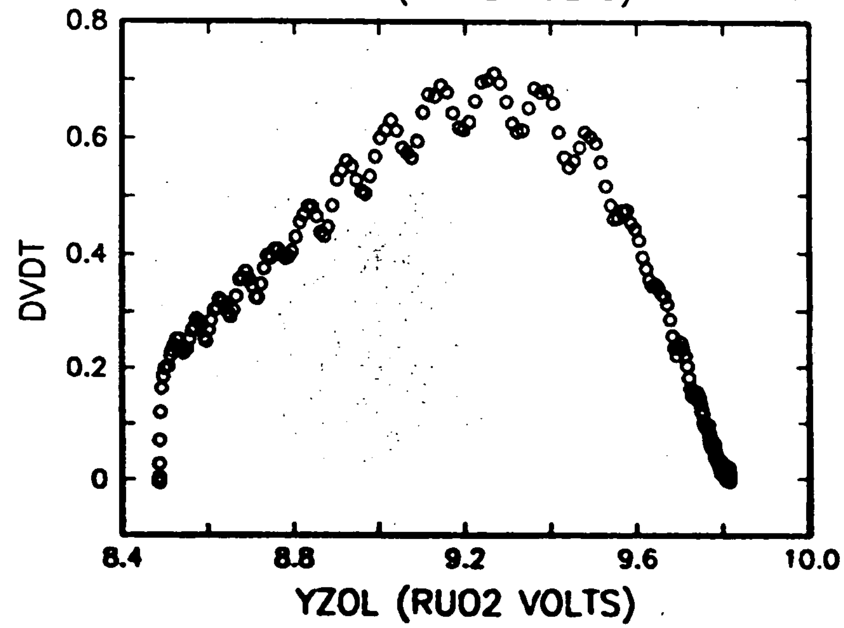


0286ZOLA.TXT

AA = 4

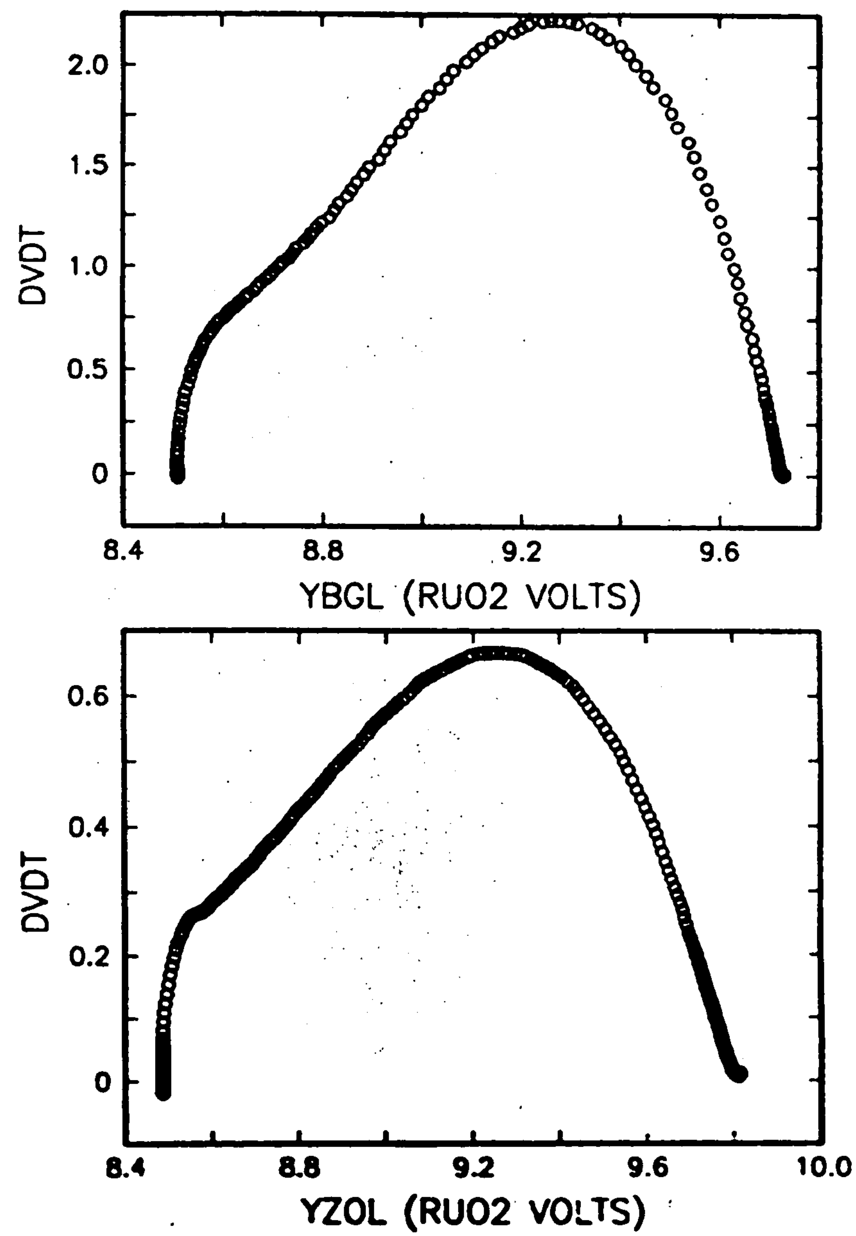


$C_B \propto \frac{1}{dV/dT}$

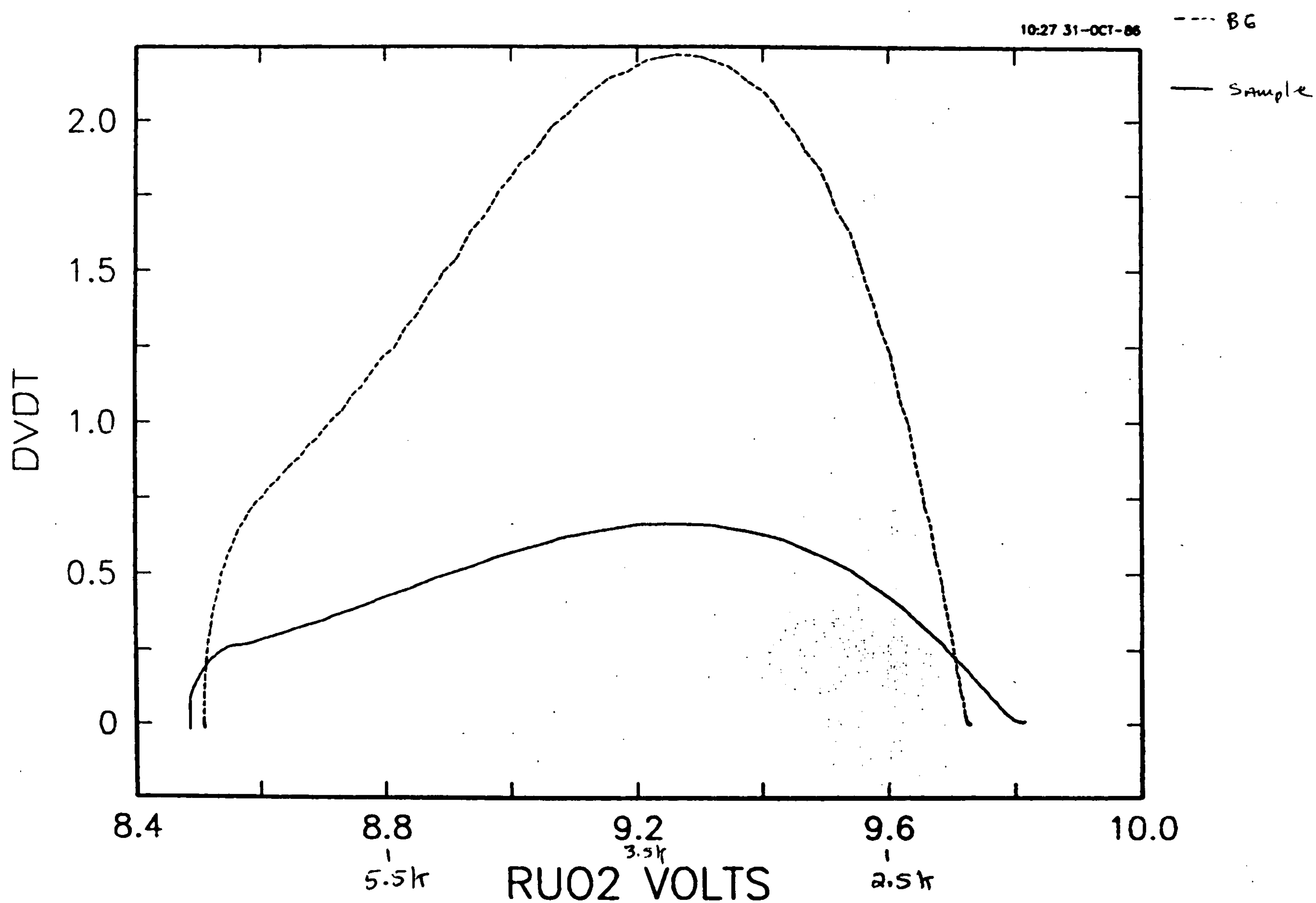


$C_S \propto \frac{1}{dV/dT}$

AA = 20

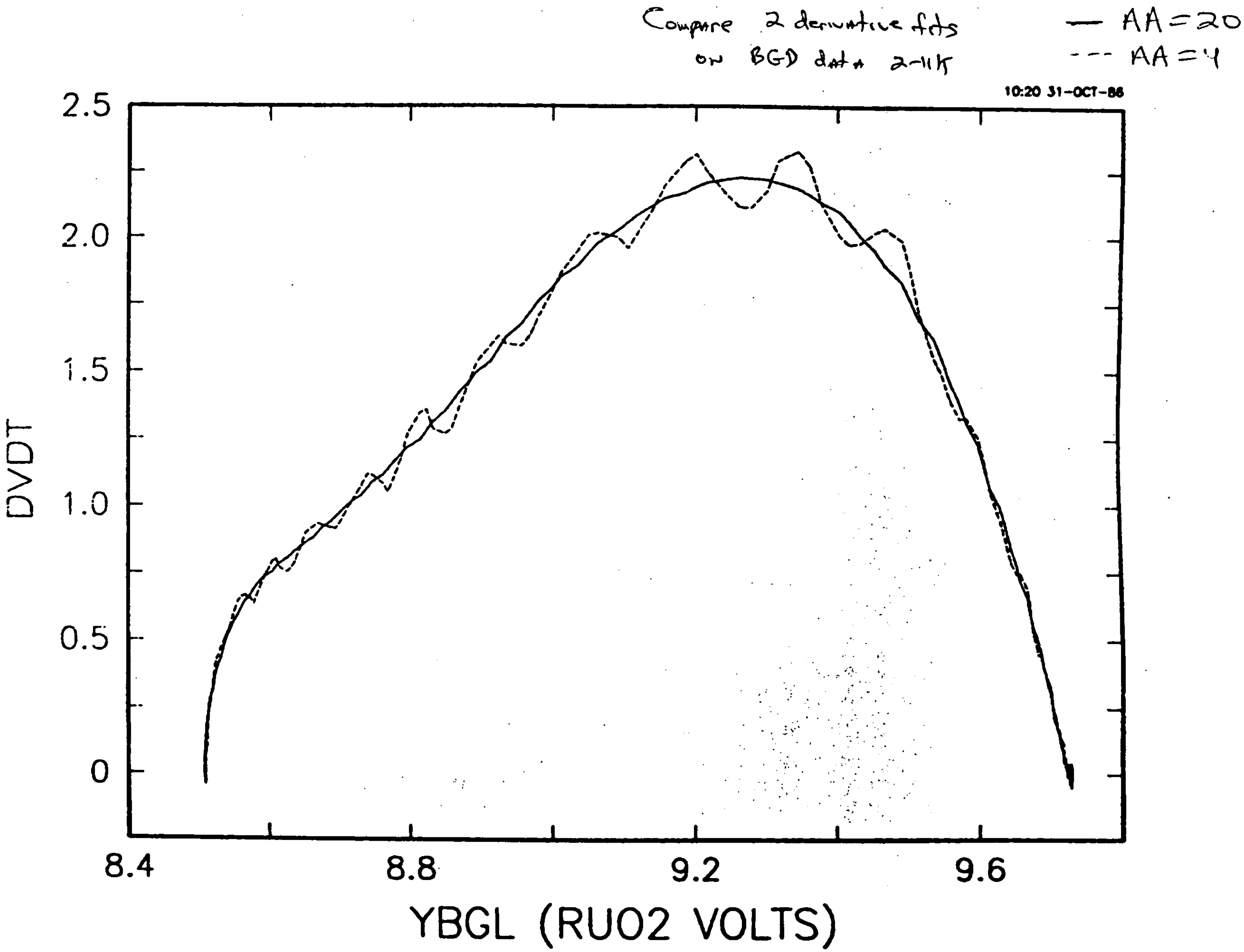

DVDT
2.0
1.5
1.0
0.5
0
8.4
8.8
9.2
9.6
YBGL (RUO2 VOLTS)
DVDT
0.6
0.4
0.2
0
8.4
8.8
9.2
9.6
10.0
YZOL (RUO2 VOLTS)

10/31/86



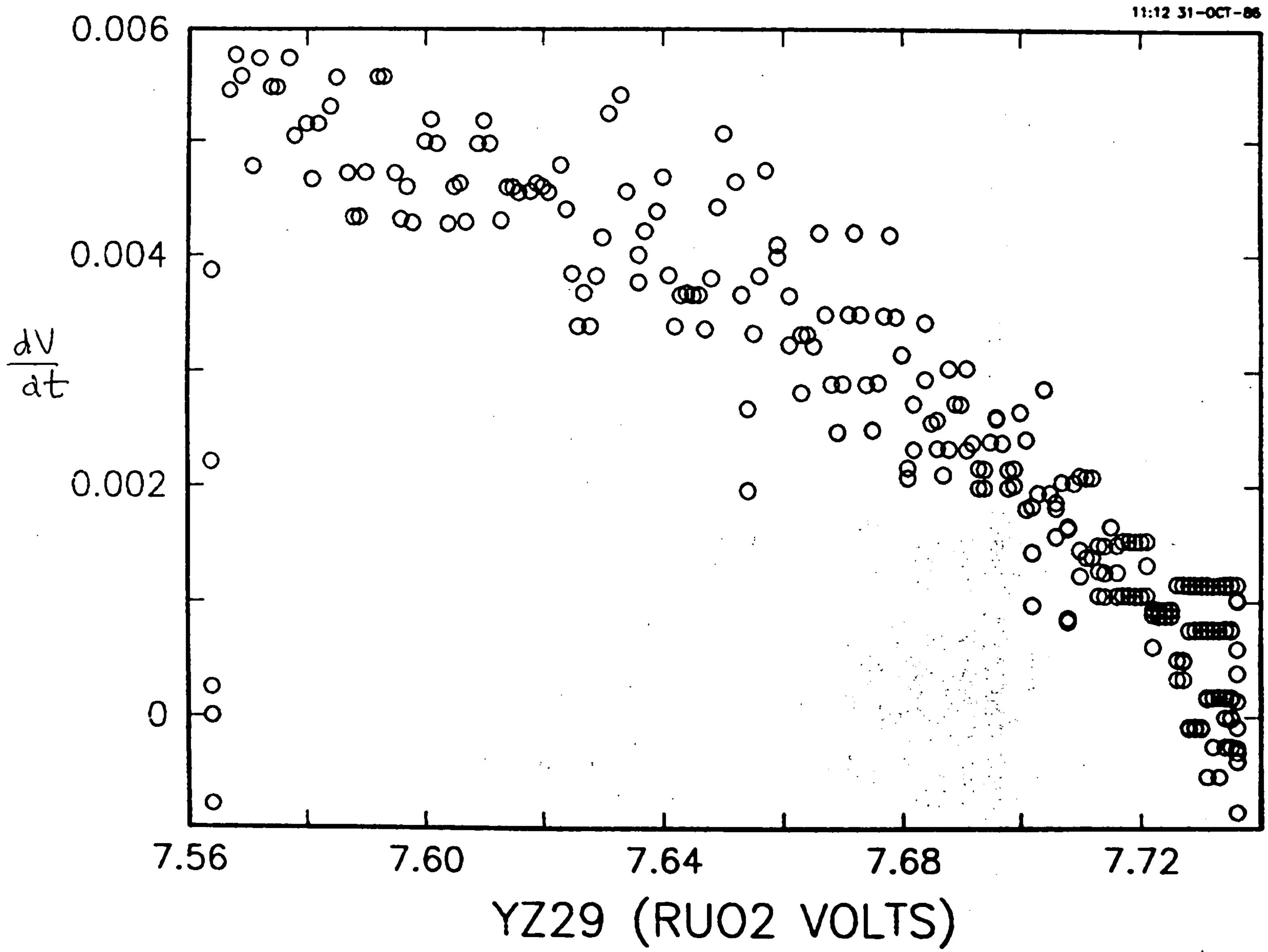
10:27 31-OCT-86
---- BG
— Sample
DVDT
2.0
1.5
1.0
0.5
0
8.4
8.8
9.2
9.6
10.0
5.5k
3.5k
2.5k
RUO2 VOLTS

9C fit
Compare 2 derivative fits
on BGD data 2-11K



2-11K BGROUND

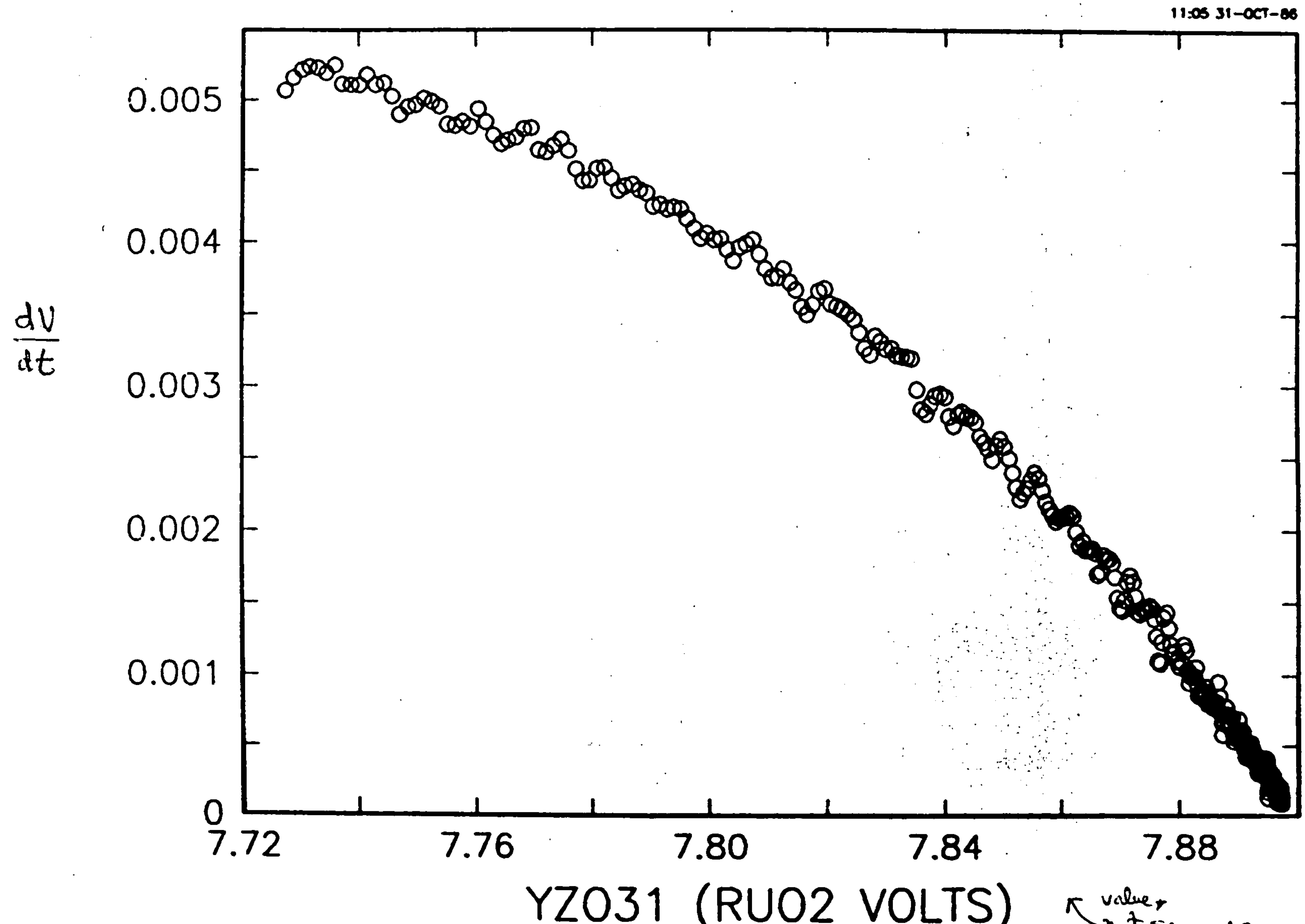
PAR Preamp 117 0296Z0HB run



AA = 4
τ_c = 100 ms

With new preamp IN PAR (116)

Noise Reduced (see next fig)



AA ← 4
$T_c = 100$ ms

values not same as previous calib. because of change of preamps.
ΔV/ΔT same

24–33 K decay

For 11/3,4 data

Title: RUO2 VS TEMP PROGRAM
Run Id. - NO36HTCB.DAT
Time and Date: 15:11:55 11-01-1986 - 17:14:40 11-01-1986
Parameter lines = 13
Min Temp to Plot = 26.00 K
Max Temp to Plot = 40.00 K
Min Volts to Plot = 7.48 Volts
Max Volts to Plot = 7.88 Volts
Plot Title = RUO2 VS TEMP
X Axis Plot Label = Sample Temp (K)
Y Axis Plot Label = RUO2 (Volts)
Start Temperature = 026 K
Temperature Step = 1.0 K
Temperature Stop = 040 K
LR400 Range = 00200 Ohms
Temperature Dev. = 0.100 K
Wait Time = 0015 seconds
Notebook messages = 4
RUO2 Calibration vs C2329 Carbon Glass Resistor
4 WIRE CONFIGURATION FOR BOLOMETER
TEMP. CALIBRATION 26-40K
STEPPING UP
Number of points = 14 Values per point = 4

RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
77.89E-01	25.95E+00	26.00E+00	0.100
78.17E-01	27.09E+00	27.00E+00	0.100
78.21E-01	28.08E+00	28.00E+00	0.100
78.11E-01	29.07E+00	29.00E+00	0.100
77.95E-01	30.07E+00	30.00E+00	0.100
77.76E-01	31.09E+00	31.00E+00	0.100
77.58E-01	32.09E+00	32.00E+00	0.100
77.41E-01	33.06E+00	33.00E+00	0.100
77.20E-01	34.01E+00	34.00E+00	0.100
77.06E-01	35.06E+00	35.00E+00	0.100
76.90E-01	36.10E+00	36.00E+00	0.100
76.75E-01	37.06E+00	37.00E+00	0.100
76.63E-01	37.92E+00	38.00E+00	0.100
76.45E-01	39.09E+00	39.00E+00	0.100

11/3,4/86 Data

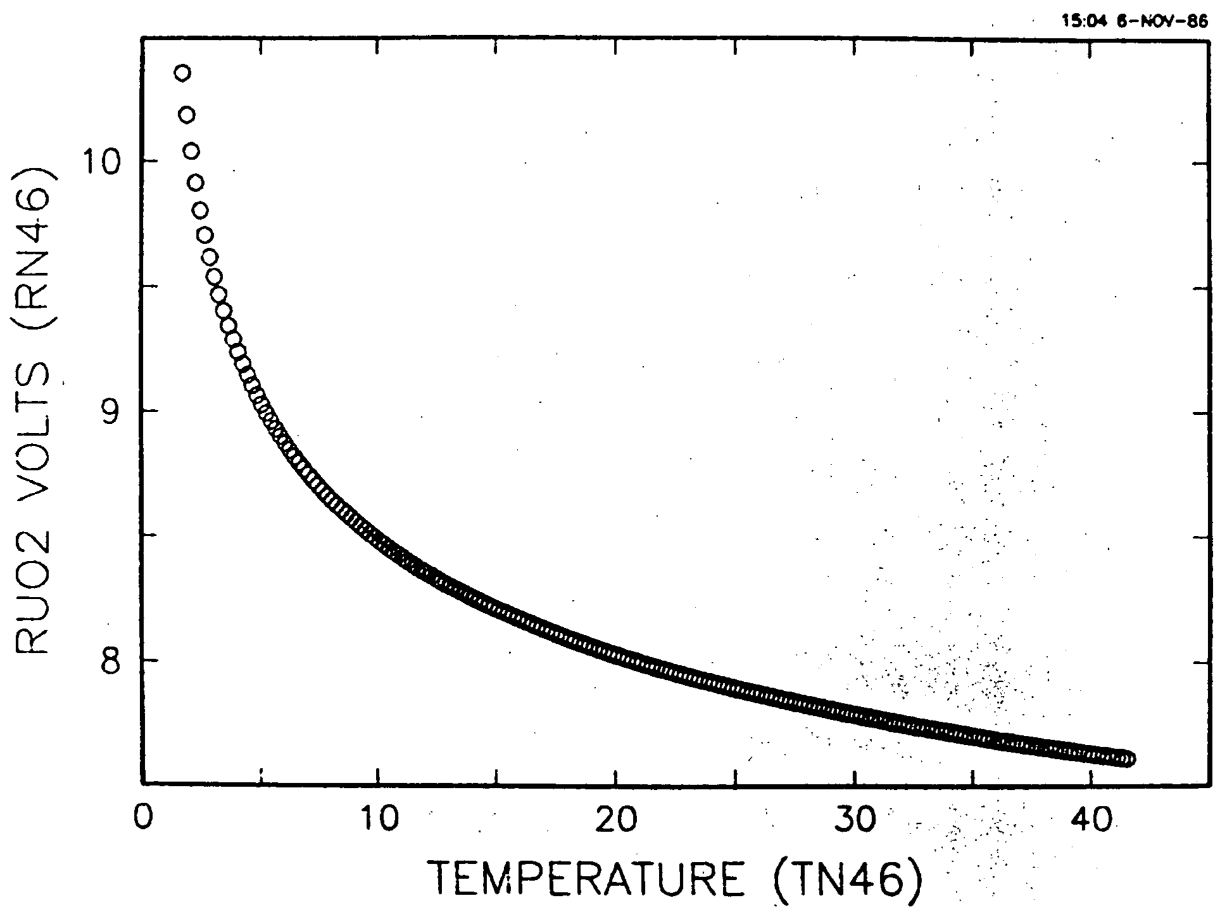
Title: RUO2 VS TEMP PROGRAM
Run Id. - NO36HTCA.DAT
Time and Date: 11:47:15 11-03-1986 - 14:56:35 11-03-1986
Parameter lines = 13
Min Temp to Plot = 05.00 K
Max Temp to Plot = 32.00 K
Min Volts to Plot = 7.58 Volts
Max Volts to Plot = 9.11 Volts
Plot Title = RUO2 VS TEMP
X Axis Plot Label = Sample Temp (K)
Y Axis Plot Label = RUO2 (Volts)
Start Temperature = 005 K
Temperature Step = 1.0 K
Temperature Stop = 032 K
LR400 Range = 02000 Ohms
Temperature Dev. = 0.050 K
Wait Time = 0010 seconds
Notebook messages = 4
RUO2 Calibration vs C2329 Carbon Glass Resistor
4 WIRE CONFIGURATION FOR BOLOMETER
TEMP. CALIBRATION 05-32K
STEPPING UP
Number of points = 27 Values per point = 4

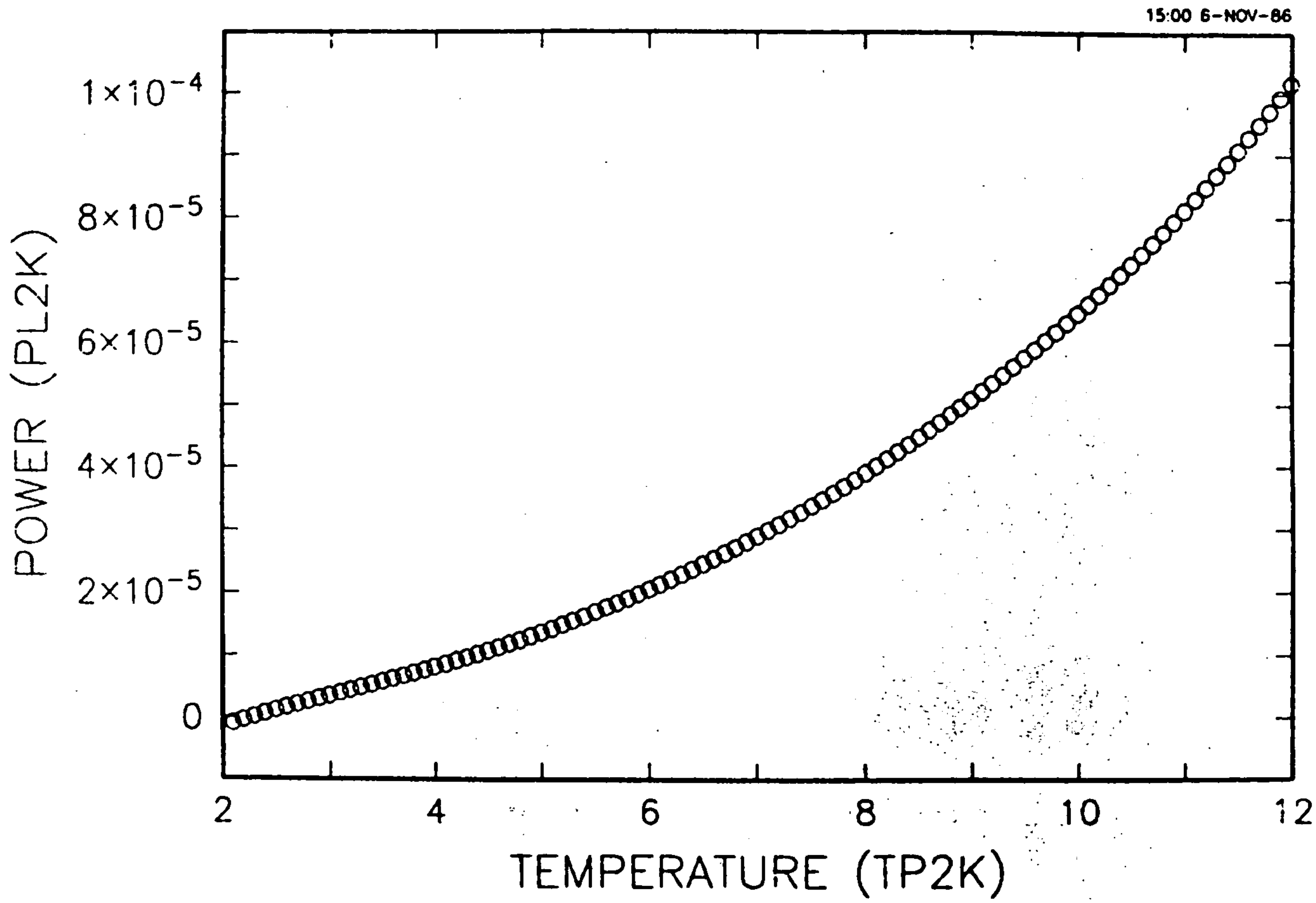
RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV	
90.57E-01	50.05E-01	50.00E-01	0.050	
88.95E-01	59.68E-01	60.00E-01	0.050	
87.66E-01	69.80E-01	70.00E-01	0.050	
86.61E-01	79.74E-01	80.00E-01	0.050	
85.71E-01	89.73E-01	90.00E-01	0.050	
84.93E-01	99.81E-01	10.00E+00	0.050	
84.25E-01	10.99E+00	11.00E+00	0.050	
83.66E-01	12.00E+00	12.00E+00	0.050	
83.13E-01	13.00E+00	13.00E+00	0.050	
82.67E-01	13.99E+00	14.00E+00	0.050	
82.17E-01	15.02E+00	15.00E+00	0.050	
81.72E-01	16.00E+00	16.00E+00	0.050	
81.33E-01	17.00E+00	17.00E+00	0.050	
80.96E-01	18.01E+00	18.00E+00	0.050	
80.62E-01	19.00E+00	19.00E+00	0.050	
80.29E-01	20.02E+00	20.00E+00	0.050	
79.99E-01	20.99E+00	21.00E+00	0.050	
79.71E-01	21.96E+00	22.00E+00	0.050	
79.44E-01	22.98E+00	23.00E+00	0.050	
79.18E-01	23.99E+00	24.00E+00	0.050	
78.94E-01	25.01E+00	25.00E+00	0.050	
78.71E-01	25.99E+00	26.00E+00	0.050	
→ 78.65E-01	27.03E+00	27.00E+00	0.050	← bad point (too high for RuO2 volts)
78.29E-01	28.03E+00	28.00E+00	0.050	
78.06E-01	28.99E+00	29.00E+00	0.050	
77.86E-01	29.97E+00	30.00E+00	0.050	
77.67E-01	30.98E+00	31.00E+00	0.050	

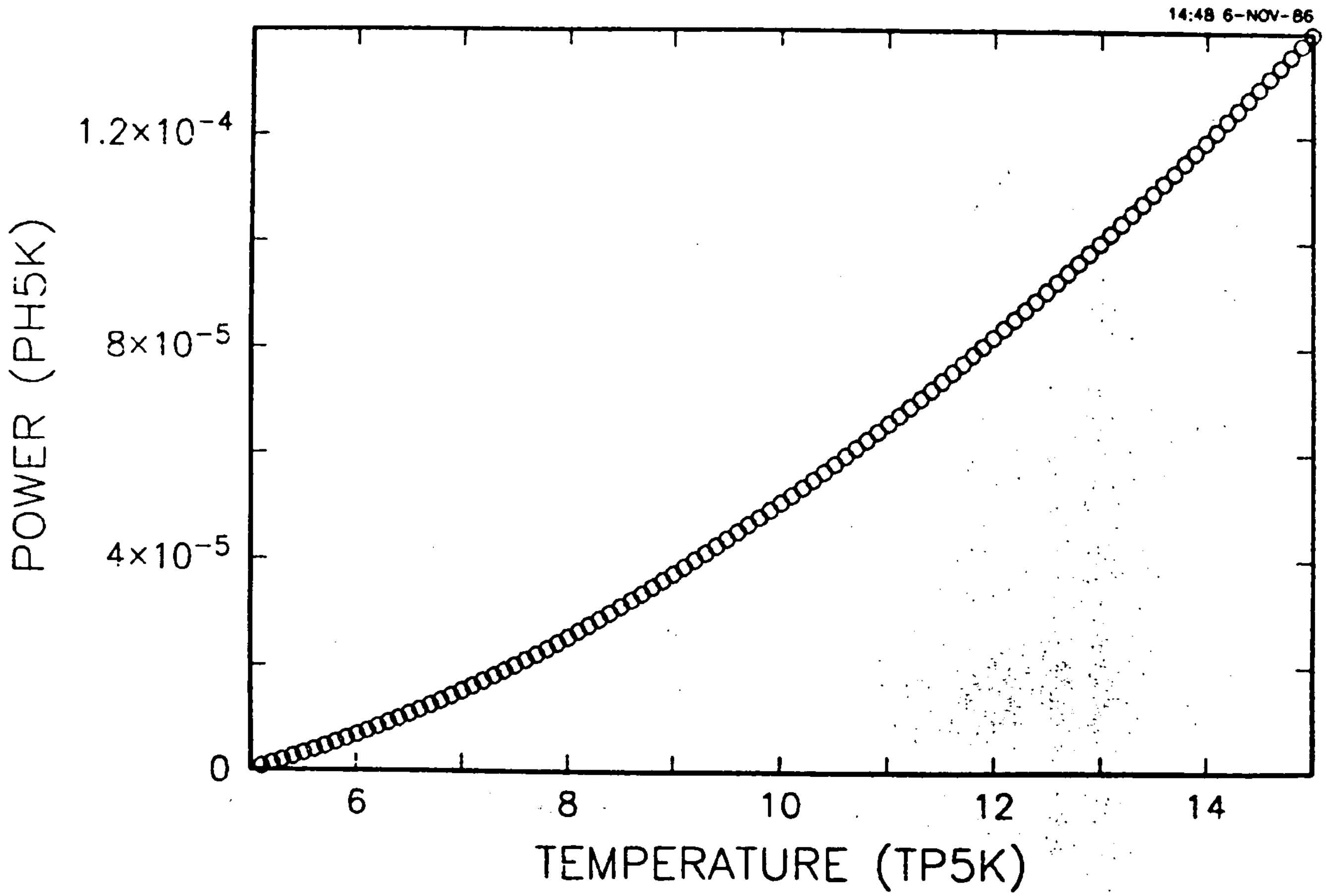
11/3,4/86 data

Title: RUO2 VS TEMP PROGRAM
Run Id. - NO46LTCA.DAT
Time and Date: 08:25:29 10-31-1986 - 09:21:20 10-31-1986
Parameter lines = 13
Min Temp to Plot = 01.60 K
Max Temp to Plot = 11.00 K
Min Volts to Plot = 8.40 Volts
Max Volts to Plot = 10.4 Volts
Plot Title = RUO2 VS TEMP
X Axis Plot Label = Sample Temp (K)
Y Axis Plot Label = RUO2 (Volts)
Start Temperature = 1.7 K
Temperature Step = 0.5 K
Temperature Stop = 011 K
LR400 Range = 20000 Ohms
Temperature Dev. = 0.050 K
Wait Time = 0010 seconds
Notebook messages = 4
RUO2 Calibration vs C2329 Carbon Glass Resistor
4 WIRE CONFIGURATION FOR BOLOMETER
TEMP. CALIBRATION 1.7-11K
STEPPING UP
Number of points = 18 Values per point = 4

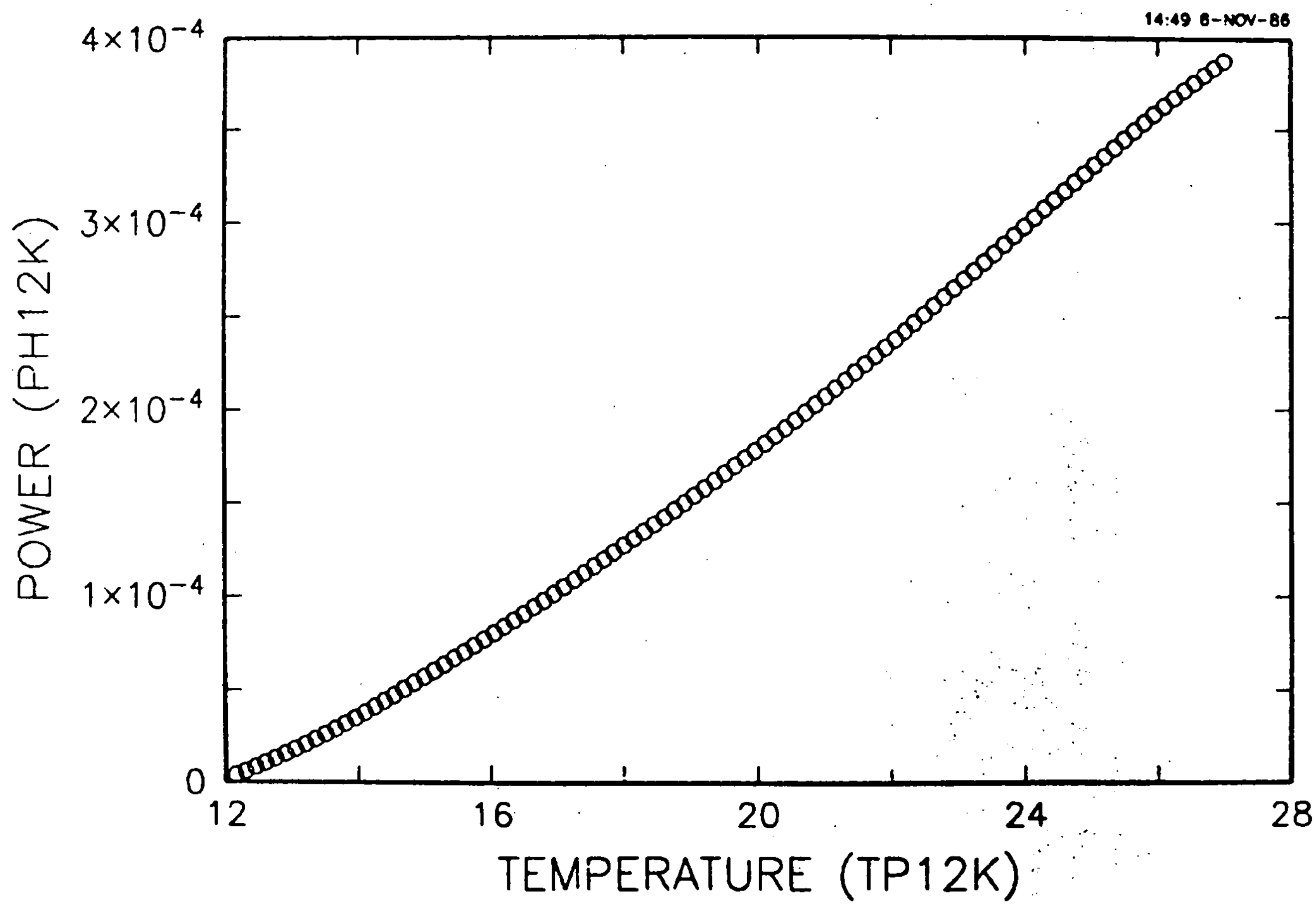
RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
10.37E+00	16.88E-01	17.00E-01	0.050
99.90E-01	21.83E-01	22.00E-01	0.050
97.09E-01	26.84E-01	27.00E-01	0.050
95.05E-01	31.84E-01	32.00E-01	0.050
93.42E-01	36.96E-01	37.00E-01	0.050
92.11E-01	42.05E-01	42.00E-01	0.050
91.21E-01	46.96E-01	47.00E-01	0.050
90.14E-01	52.04E-01	52.00E-01	0.050
89.30E-01	57.19E-01	57.00E-01	0.050
88.57E-01	62.17E-01	62.00E-01	0.050
87.92E-01	67.16E-01	67.00E-01	0.050
87.32E-01	71.94E-01	72.00E-01	0.050
86.79E-01	76.82E-01	77.00E-01	0.050
86.31E-01	81.74E-01	82.00E-01	0.050
85.85E-01	86.80E-01	87.00E-01	0.050
85.44E-01	91.90E-01	92.00E-01	0.050
85.03E-01	97.25E-01	97.00E-01	0.050
84.70E-01	10.23E+00	10.20E+00	0.050

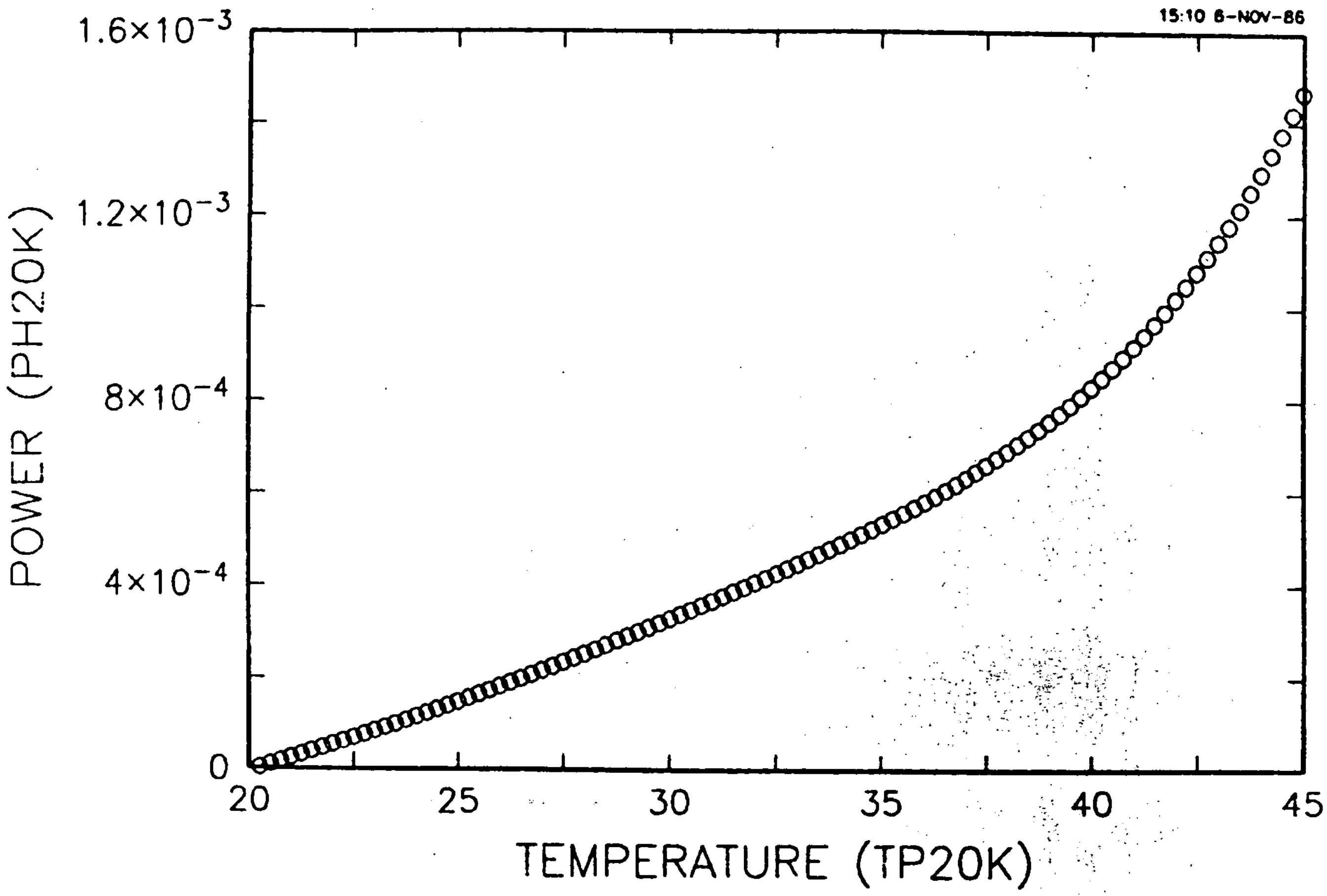

15:04 6-NOV-86
RUO2 VOLTS (RN46)
10
9
8
0
10
20
30
40
TEMPERATURE (TN46)

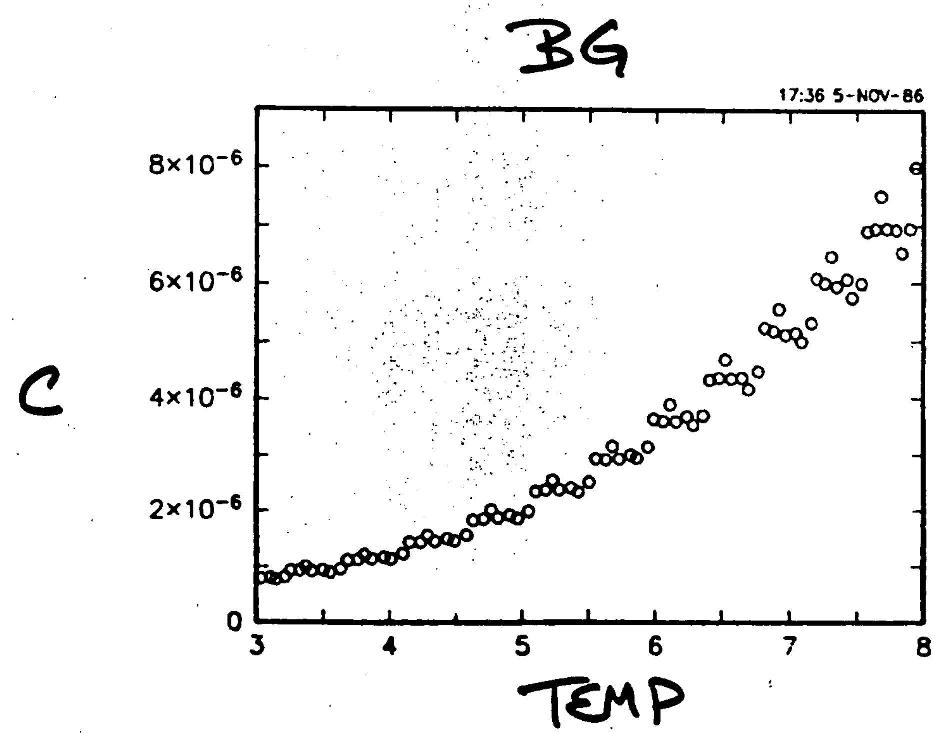

15:00 6-NOV-86
POWER (PL2K)
1×10⁻⁴
8×10⁻⁵
6×10⁻⁵
4×10⁻⁵
2×10⁻⁵
0
2
4
6
8
10
12
TEMPERATURE (TP2K)



14:48 6-NOV-86
POWER (PH5K)
1.2×10⁻⁴
8×10⁻⁵
4×10⁻⁵
0
6
8
10
12
14
TEMPERATURE (TP5K)


14:49 6-NOV-86
POWER (PH12K)
4×10⁻⁴
3×10⁻⁴
2×10⁻⁴
1×10⁻⁴
0
12
16
20
24
28
TEMPERATURE (TP12K)

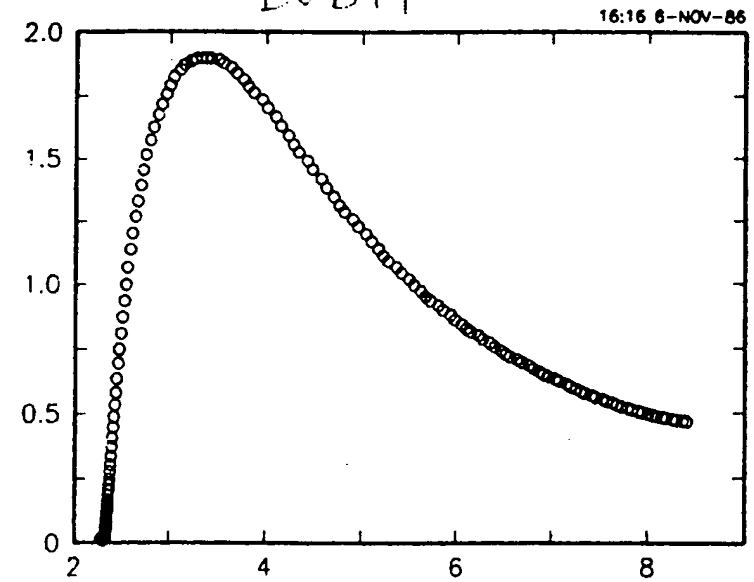

15:10 6-NOV-86
1.6×10⁻³
1.2×10⁻³
8×10⁻⁴
4×10⁻⁴
0
20
25
30
35
40
45
POWER (PH20K)
TEMPERATURE (TP20K)



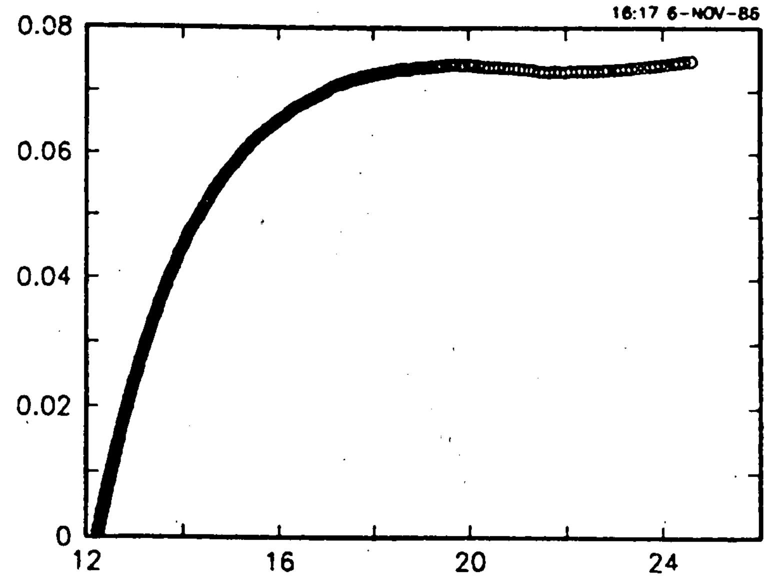
AA = 4

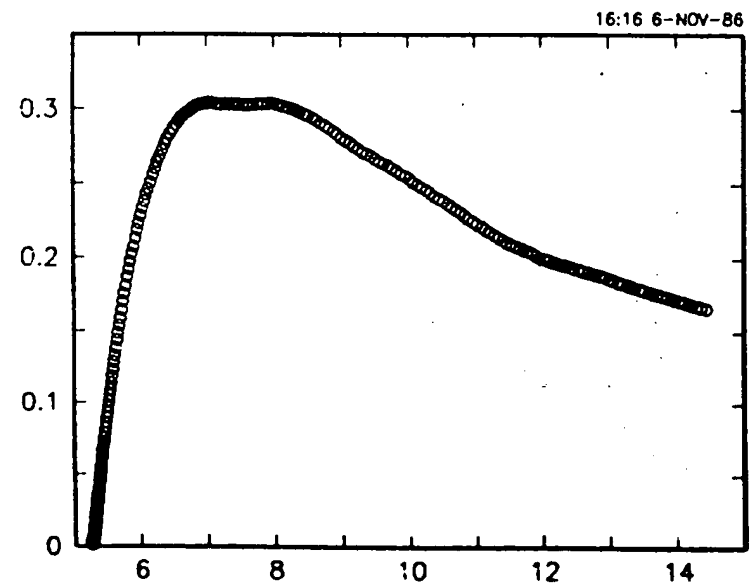
BACKGROUND

DVDT1

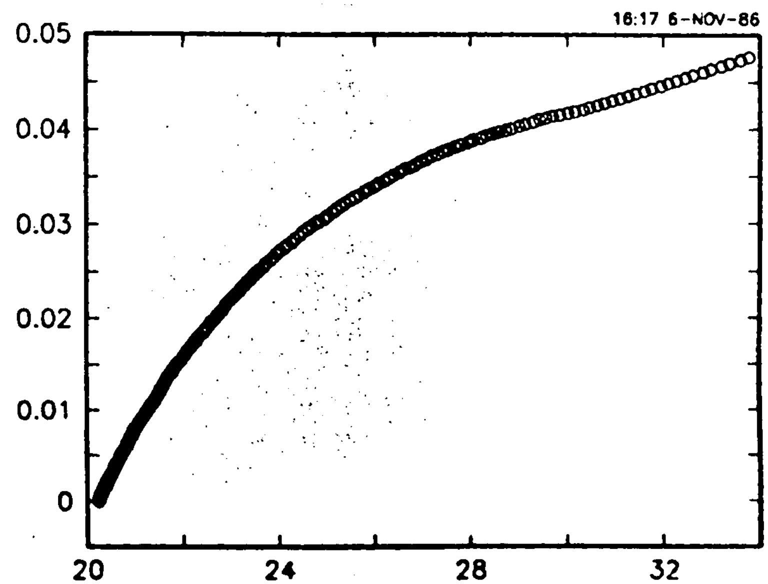


DV DT 3



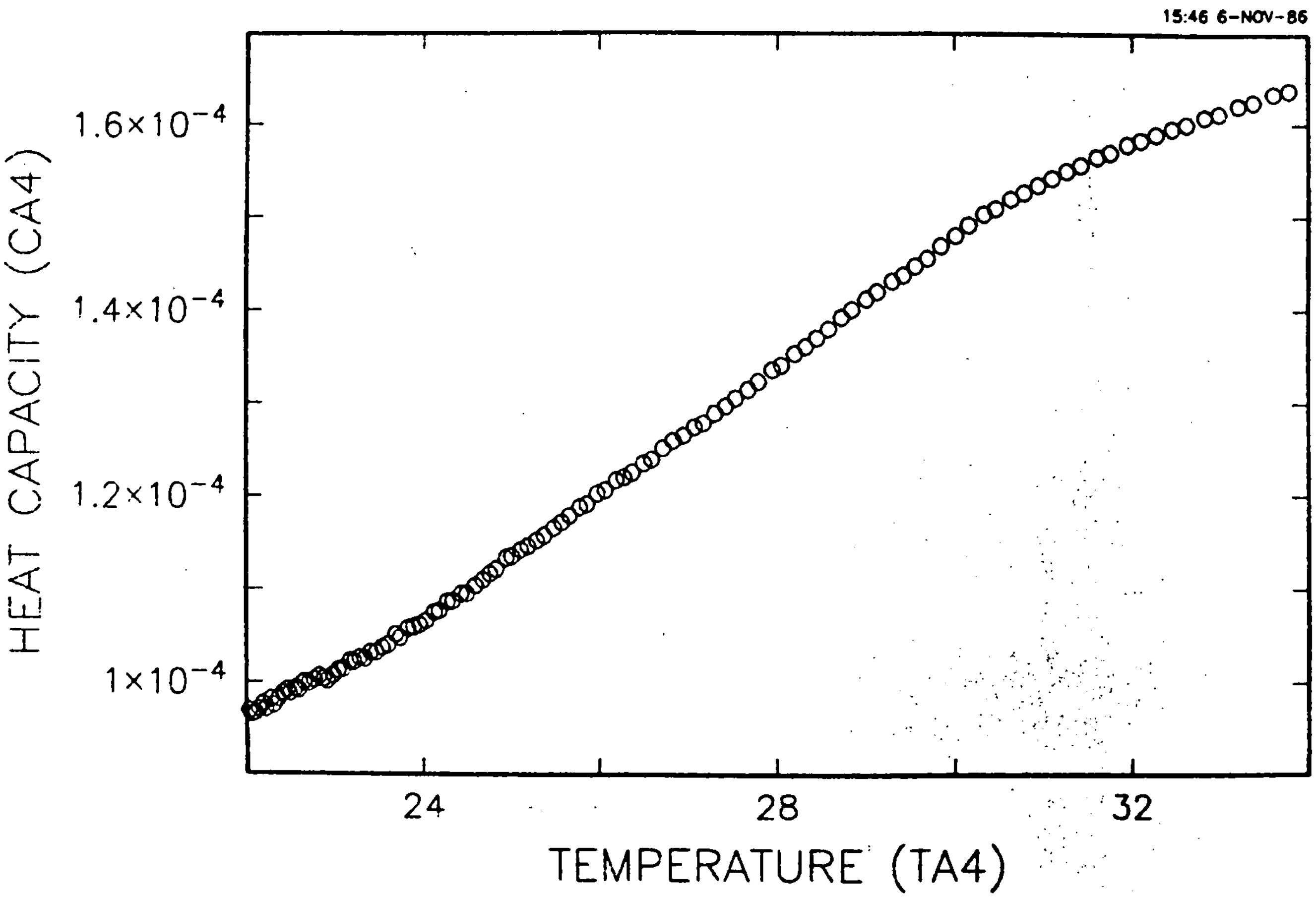


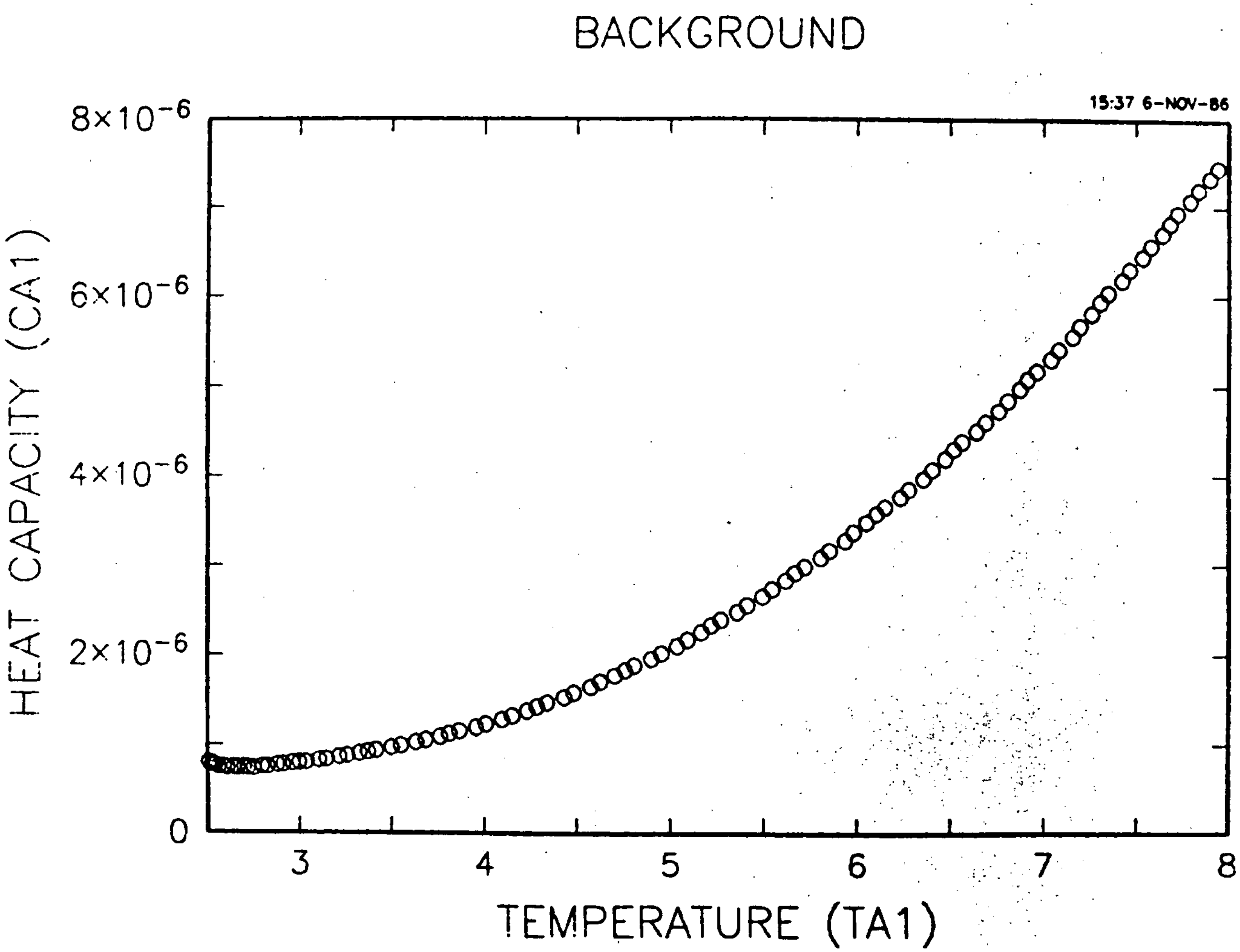
DV DT 2

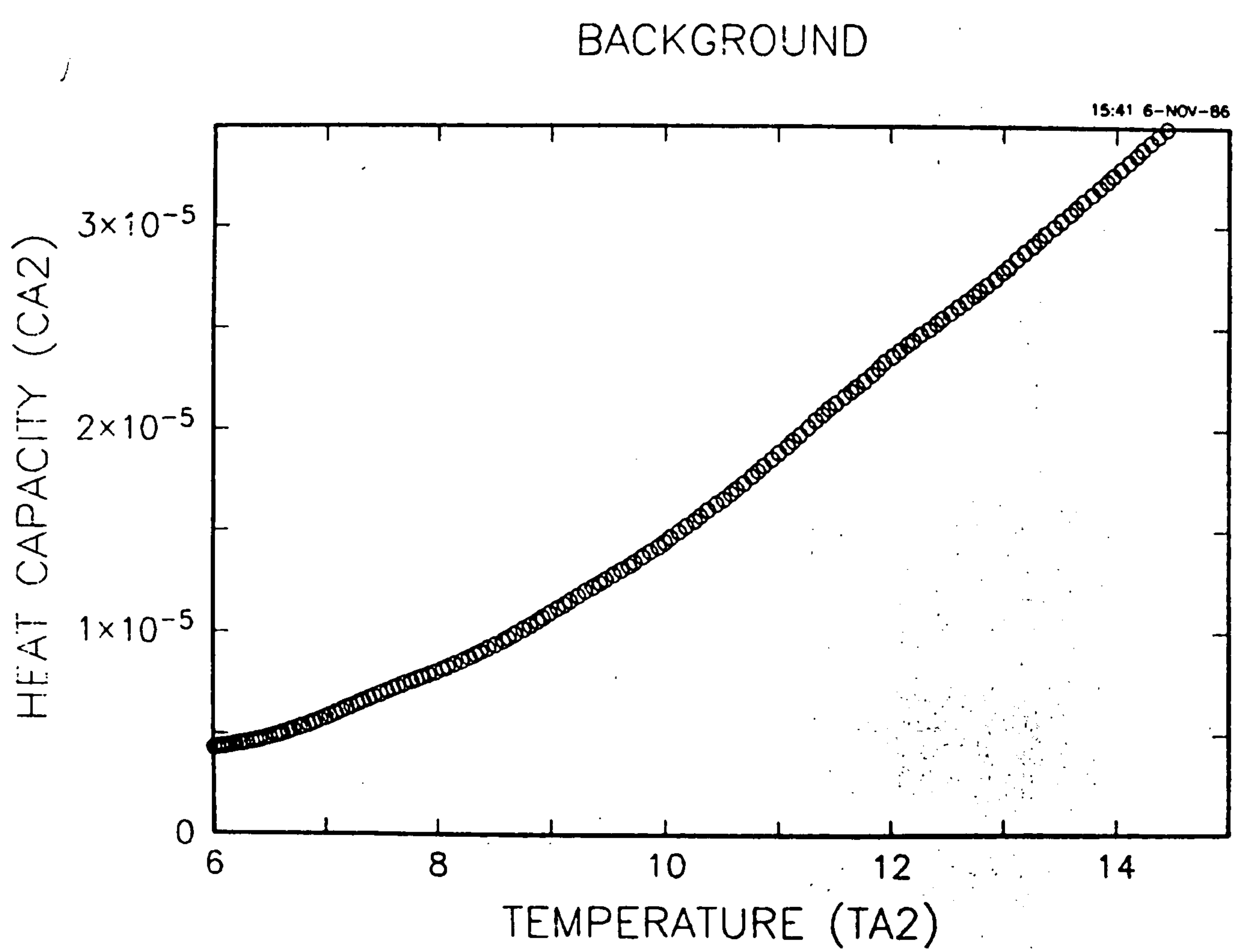


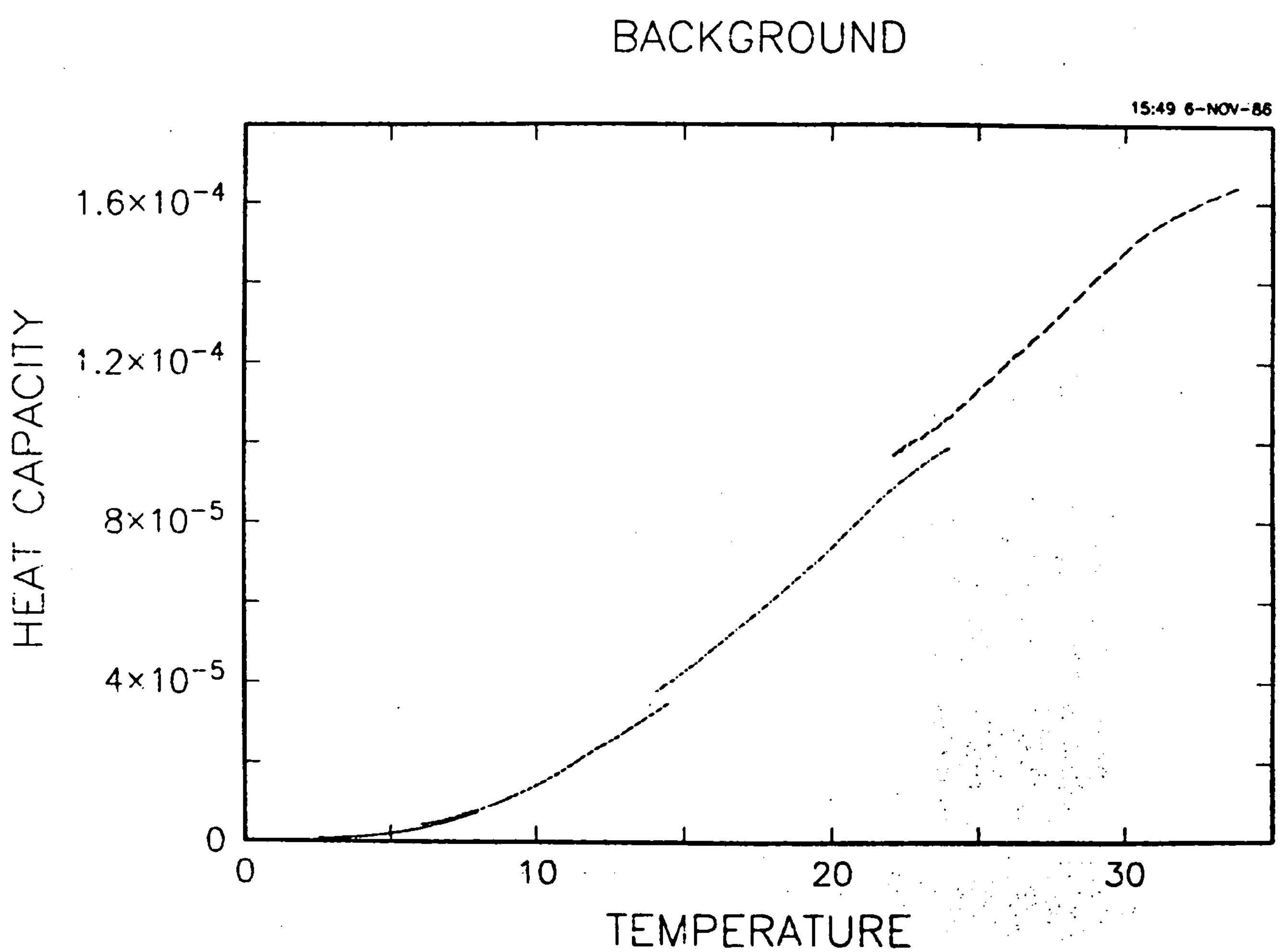
DVDT 4

BACKGROUND

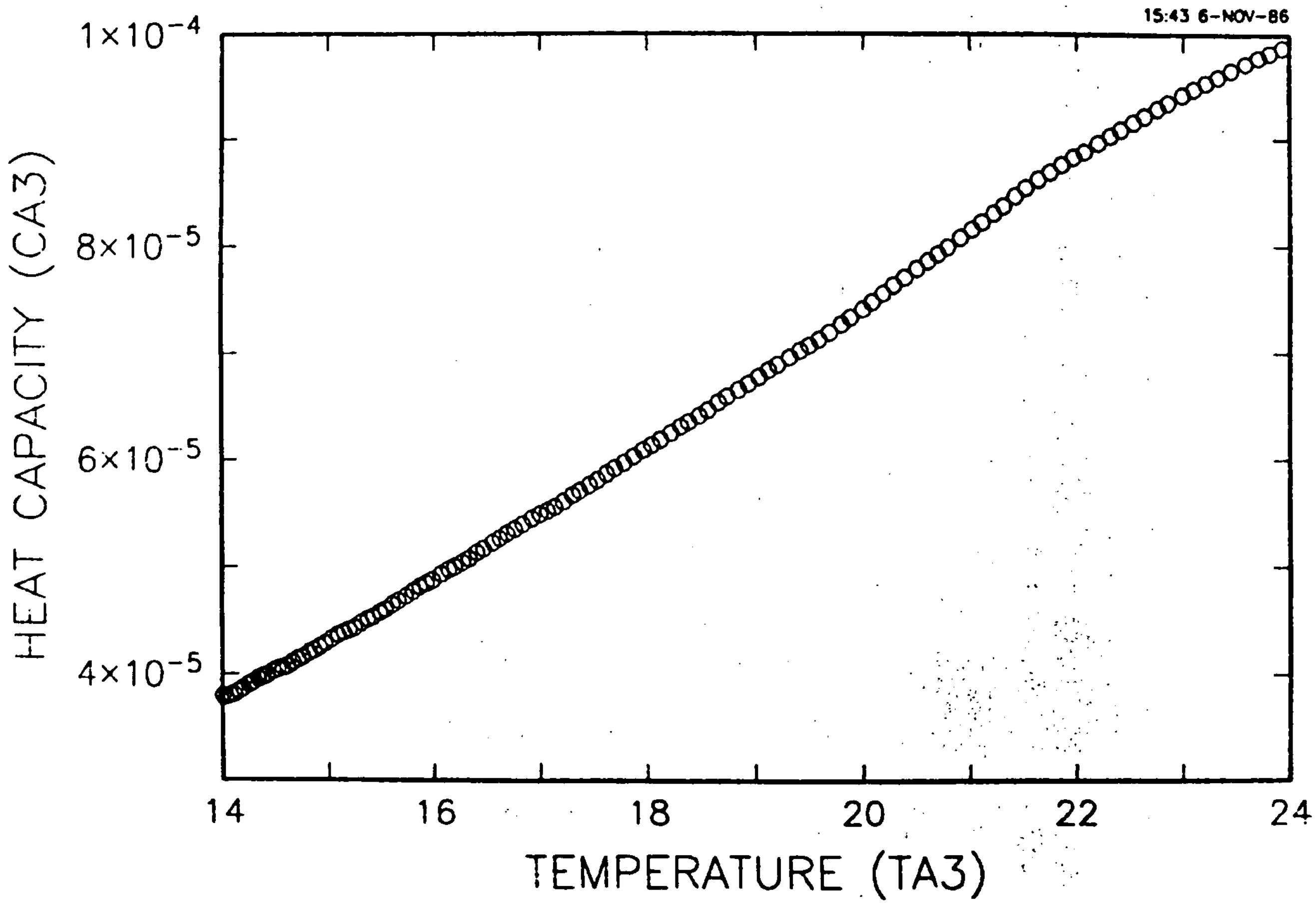

15:46 6-NOV-86
HEAT CAPACITY (CA4)
1.6×10⁻⁴
1.4×10⁻⁴
1.2×10⁻⁴
1×10⁻⁴
24
28
32
TEMPERATURE (TA4)

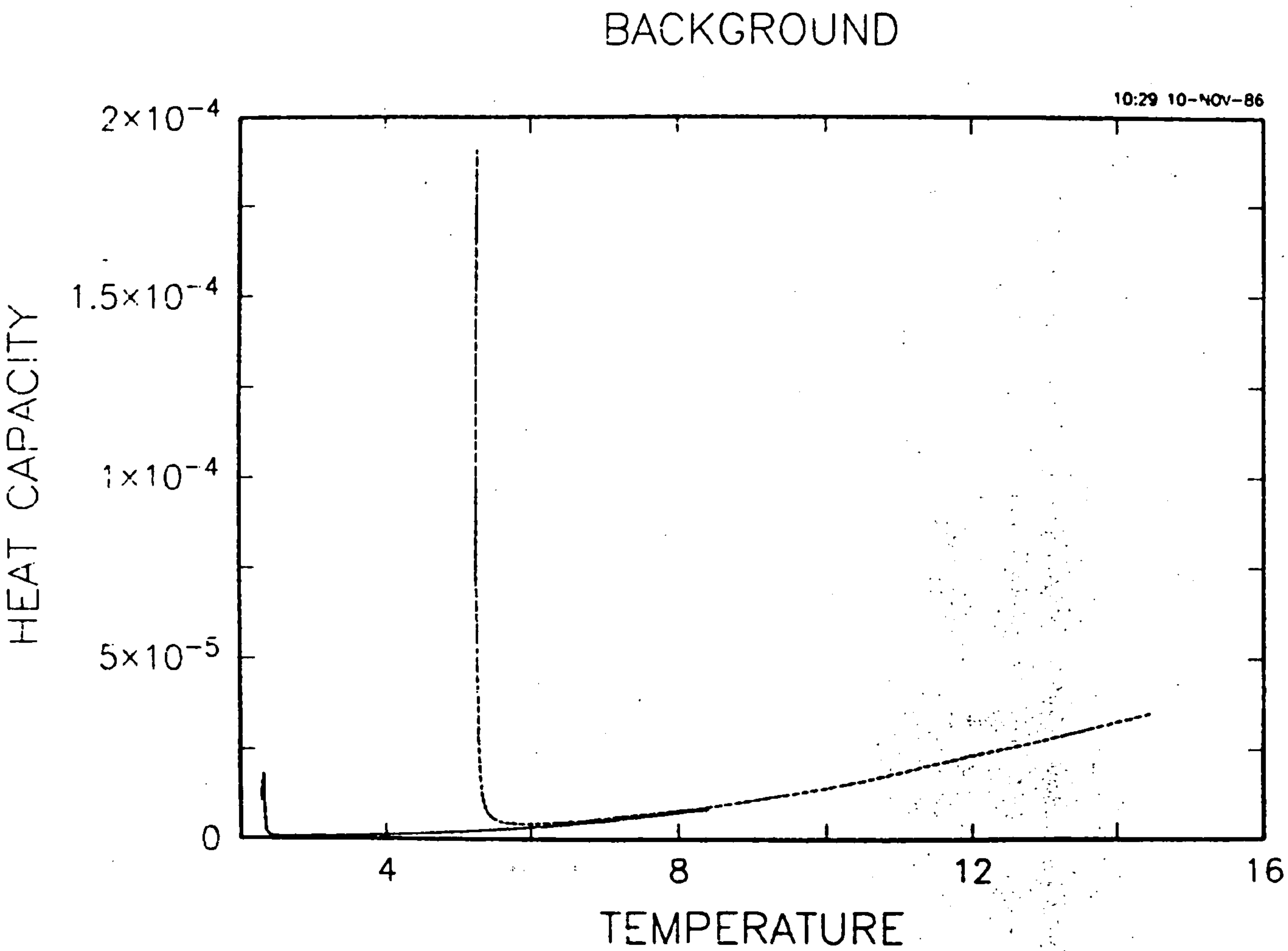

BACKGROUND
15:37 6-NOV-86
HEAT CAPACITY (CA1)
8×10^-6
6×10^-6
4×10^-6
2×10^-6
0
3
4
5
6
7
8
TEMPERATURE (TA1)


BACKGROUND
15:41 6-NOV-86
HEAT CAPACITY (CA2)
3×10^-5
2×10^-5
1×10^-5
0
6
8
10
12
14
TEMPERATURE (TA2)


BACKGROUND
15:49 6-NOV-86
HEAT CAPACITY
1.6×10^-4
1.2×10^-4
8×10^-5
4×10^-5
0
0
10
20
30
TEMPERATURE

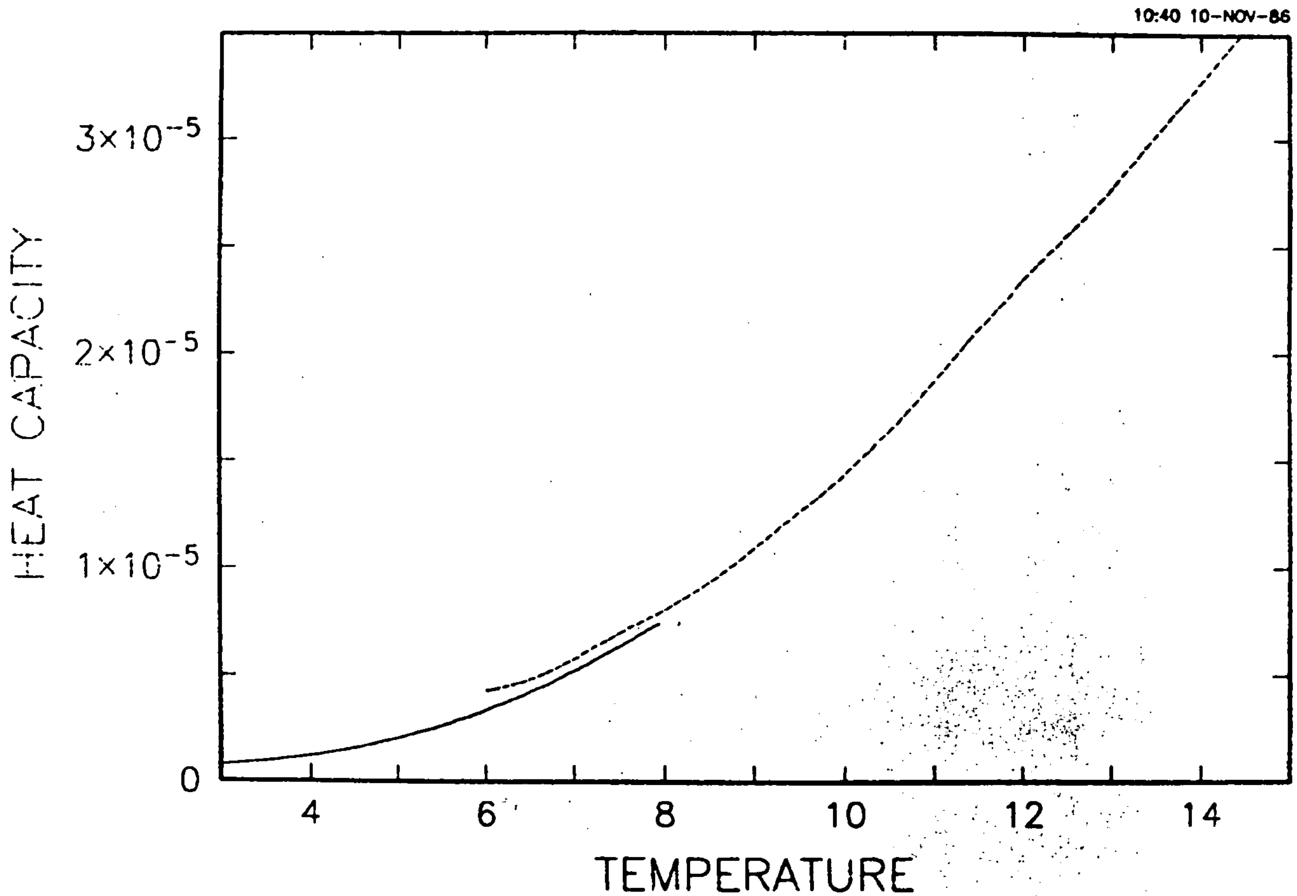
BACKGROUND

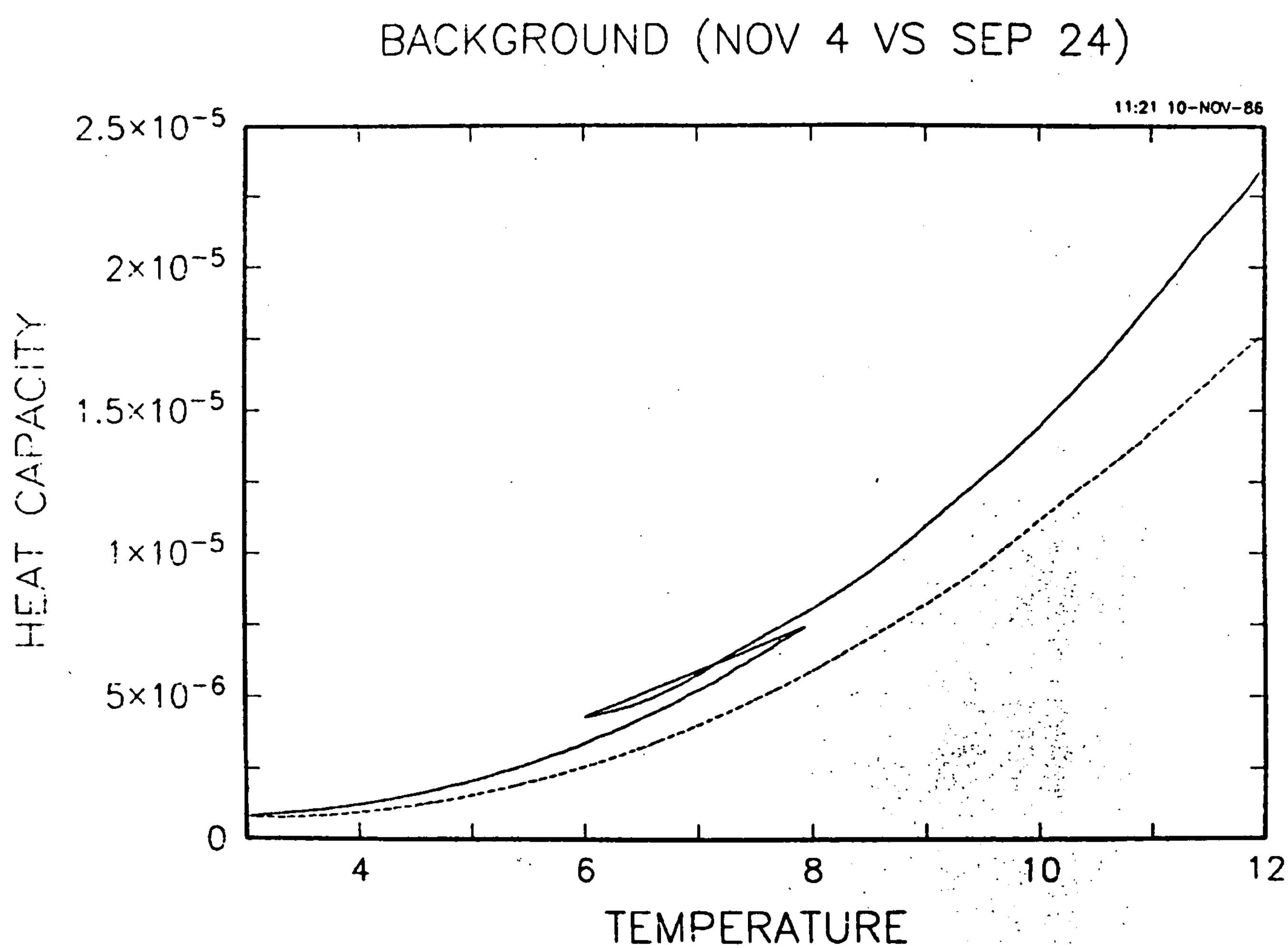

15:43 6-NOV-86
1×10^-4
8×10^-5
6×10^-5
4×10^-5
HEAT CAPACITY (CA3)
14
16
18
20
22
24
TEMPERATURE (TA3)

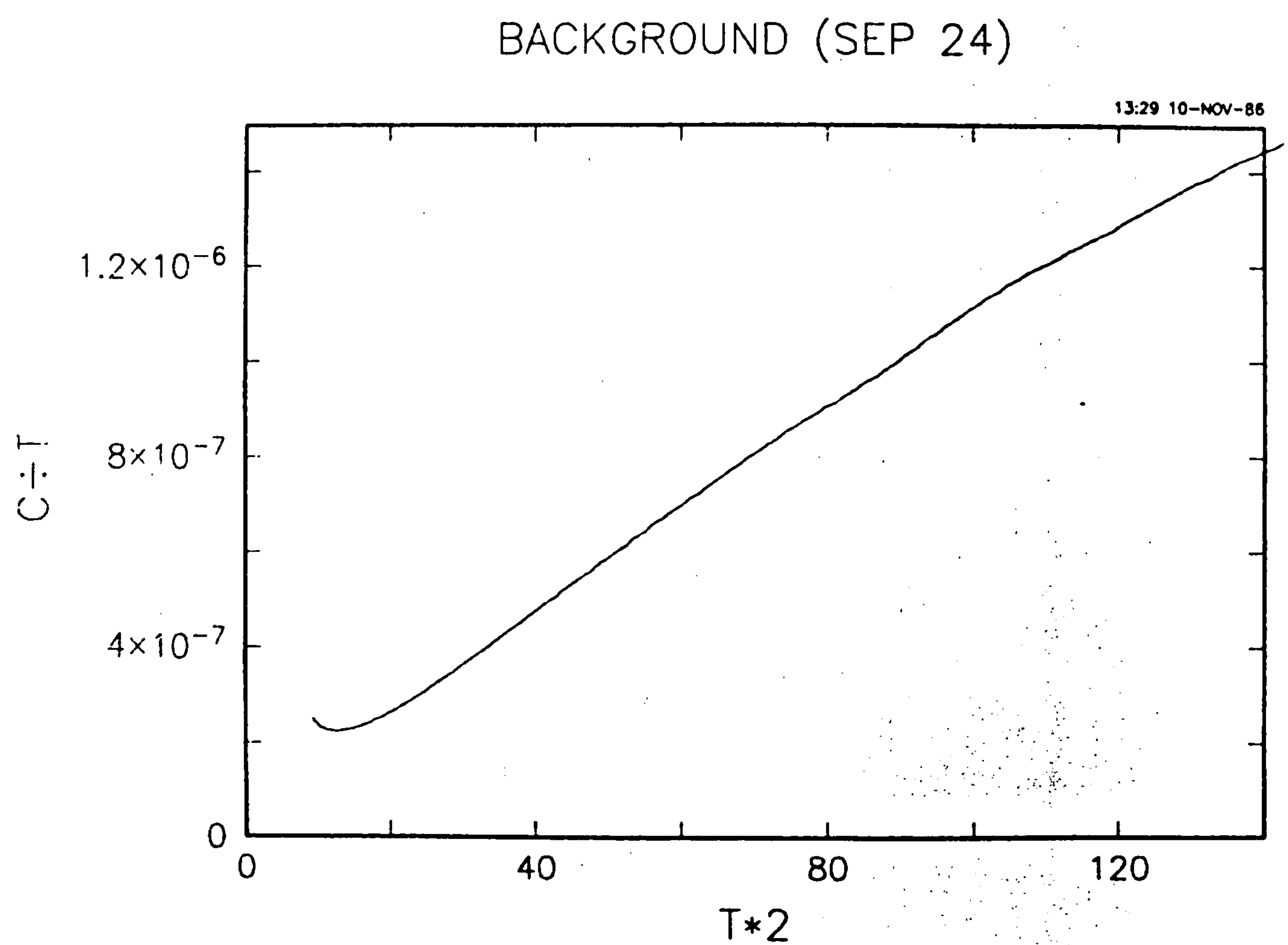


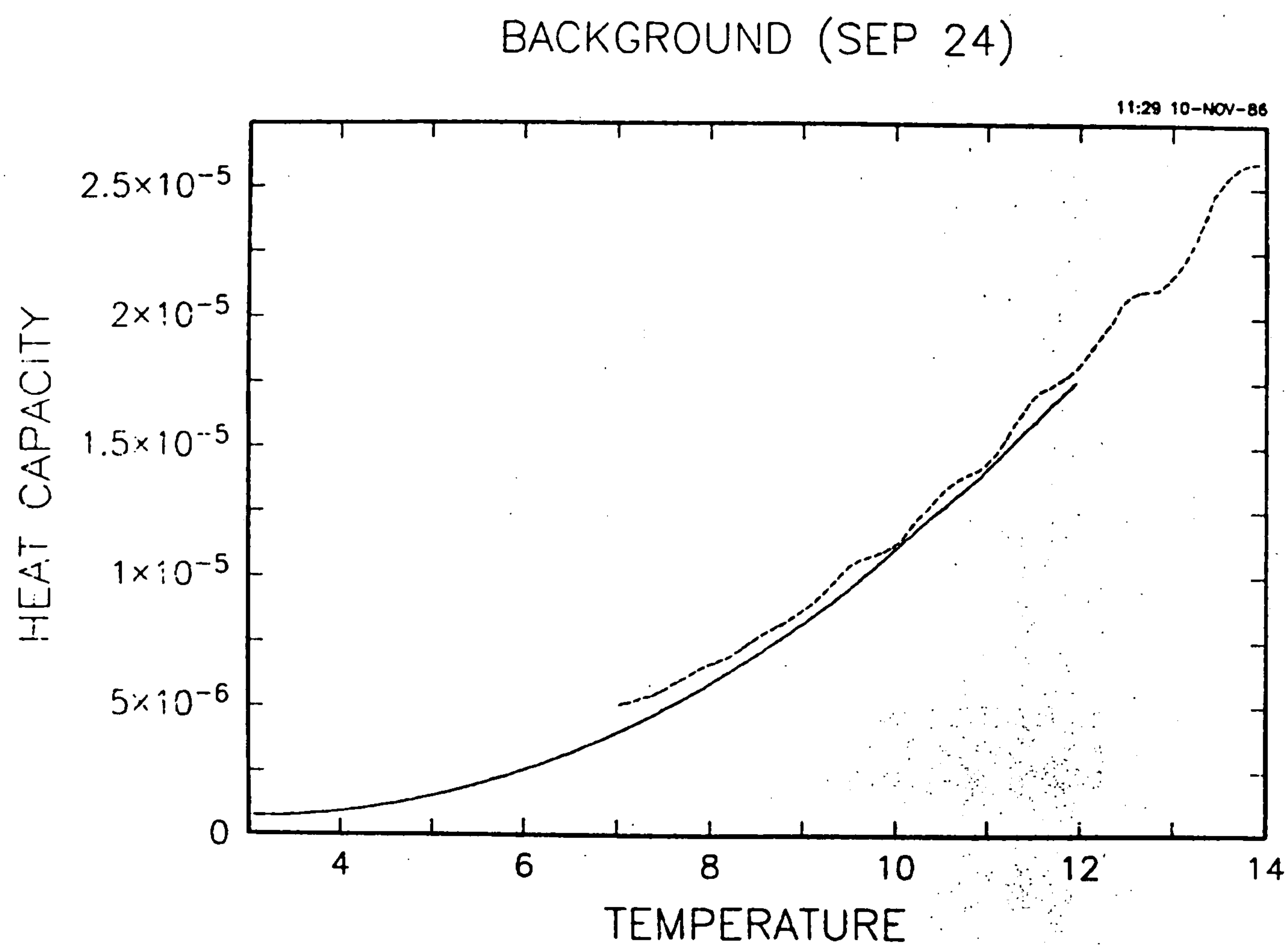
BACKGROUND
10:29 10-NOV-86
HEAT CAPACITY
2×10⁻⁴
1.5×10⁻⁴
1×10⁻⁴
5×10⁻⁵
0
4
8
12
16
TEMPERATURE

BACKGROUND (NOV 4)

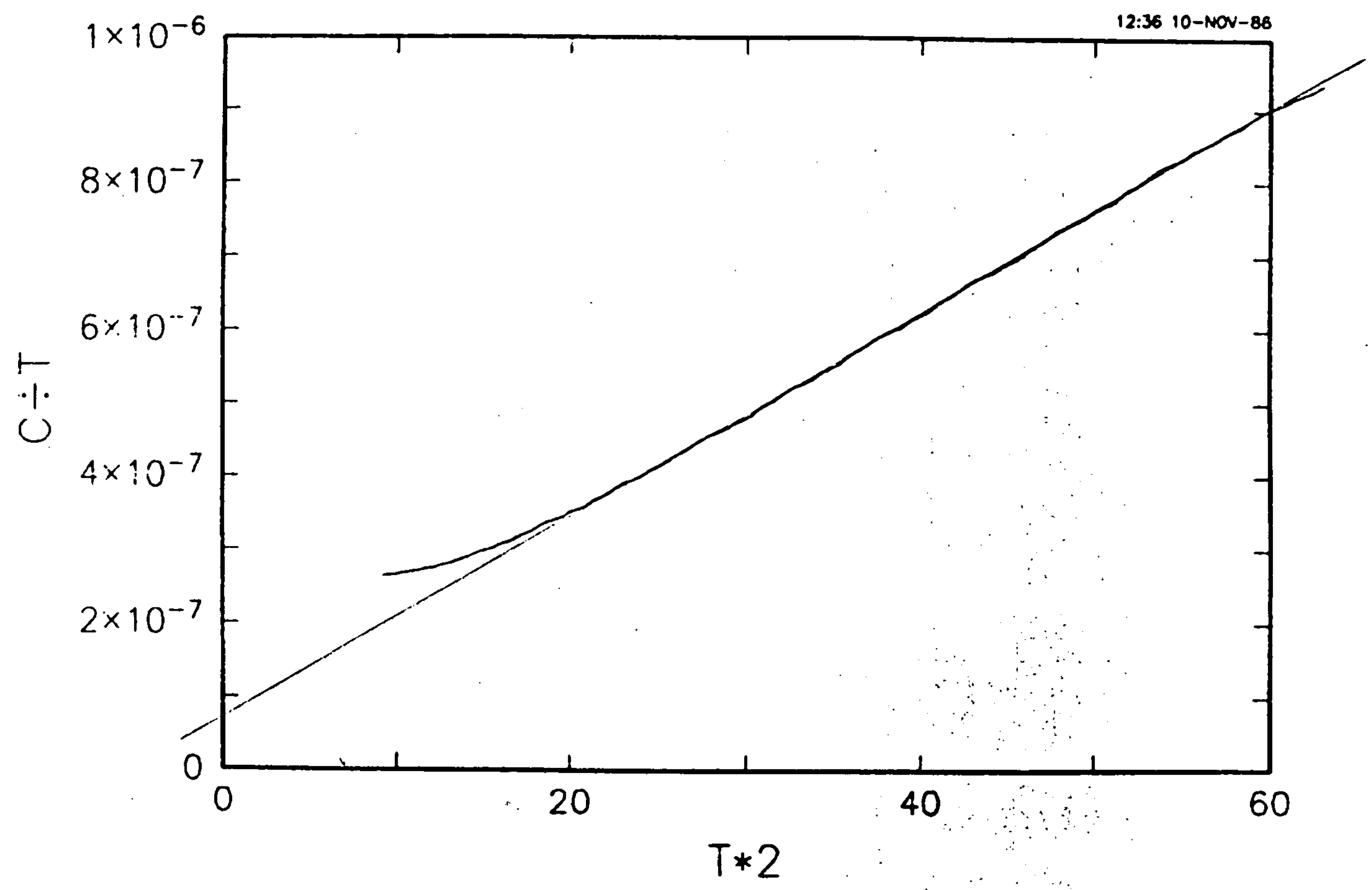


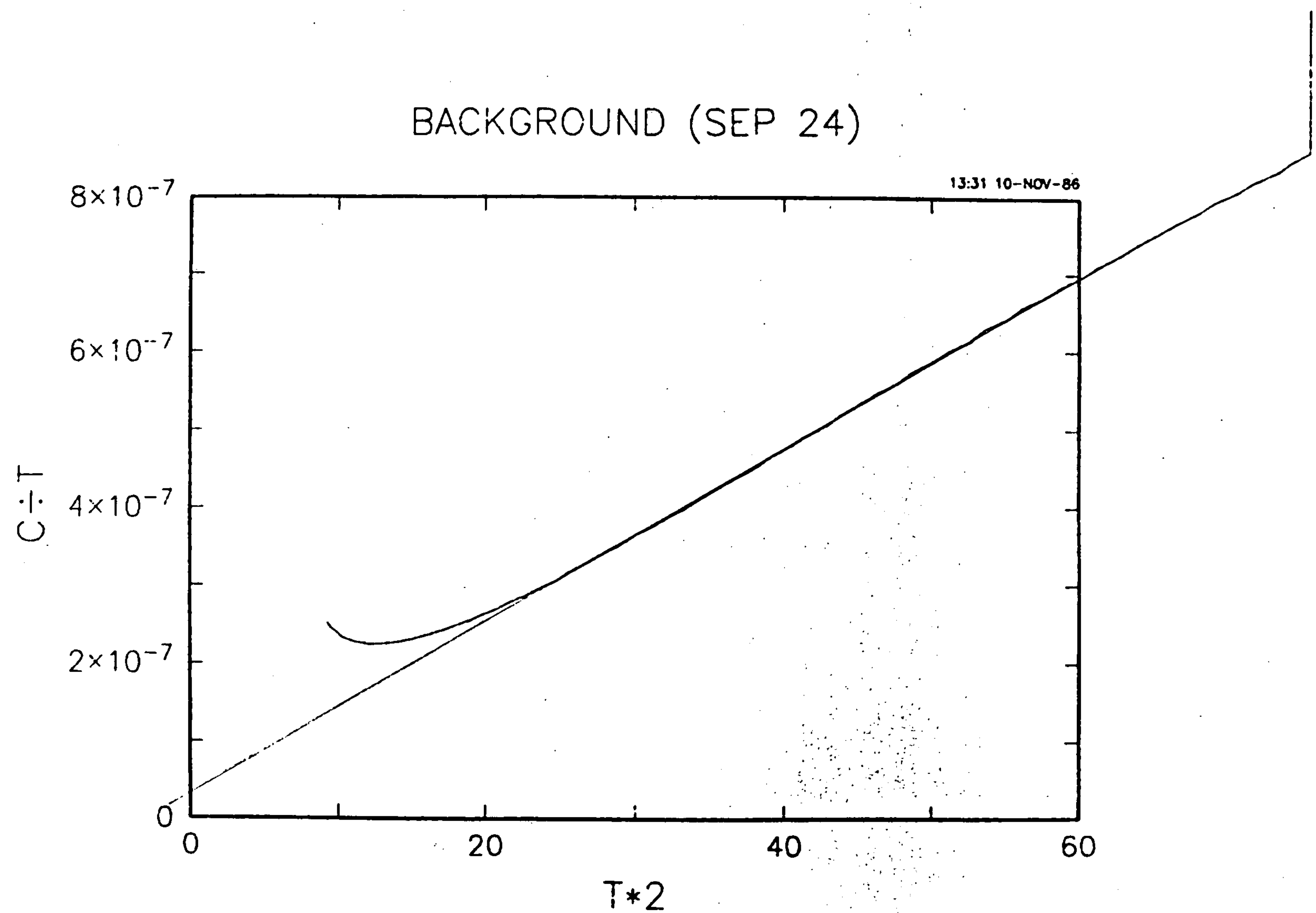

BACKGROUND (NOV 4 VS SEP 24)
11:21 10-NOV-86
HEAT CAPACITY
2.5×10⁻⁵
2×10⁻⁵
1.5×10⁻⁵
1×10⁻⁵
5×10⁻⁶
0
4
6
8
10
12
TEMPERATURE

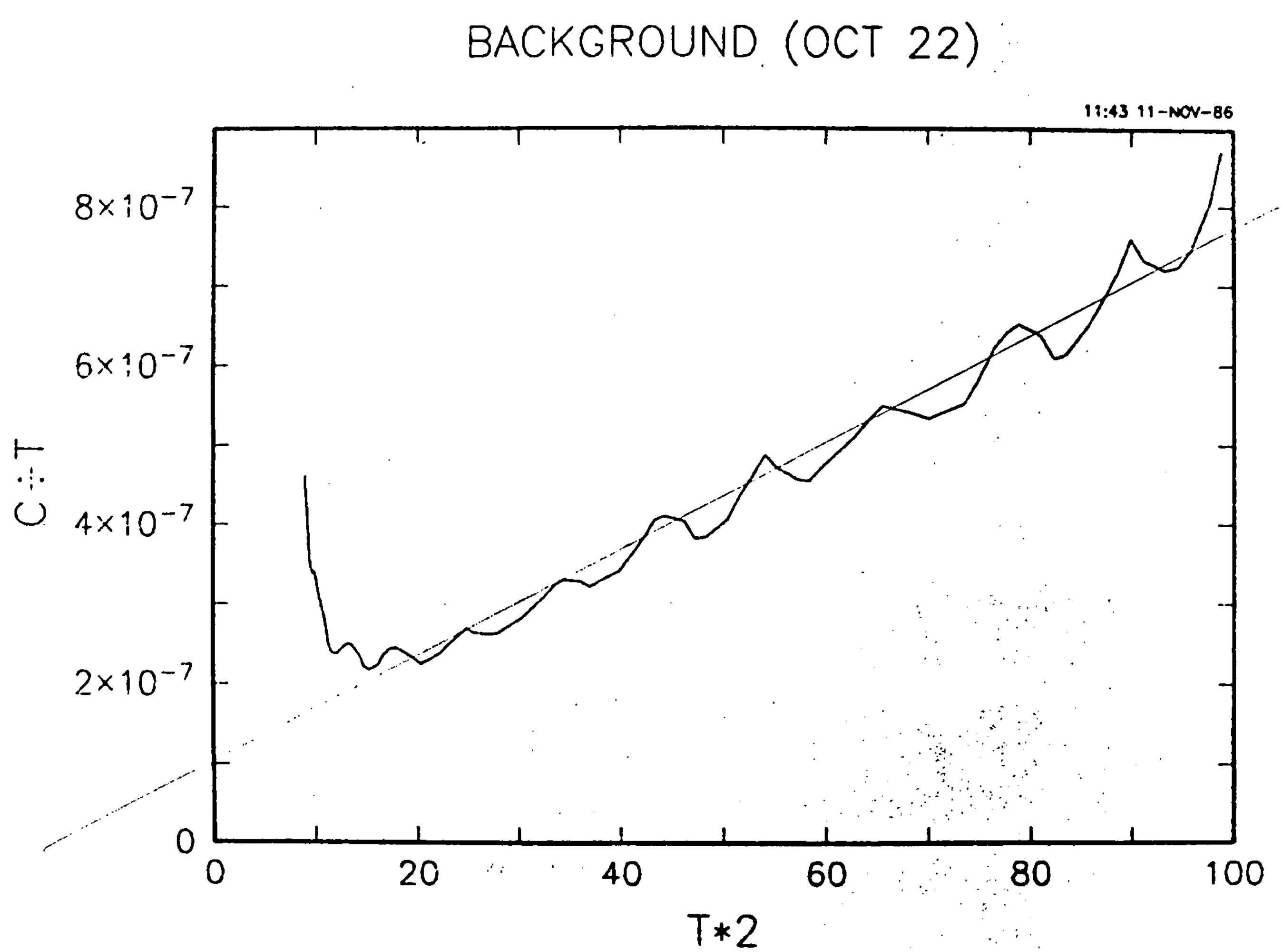

BACKGROUND (SEP 24)
13:29 10-NOV-86
C÷T
1.2×10⁻⁶
8×10⁻⁷
4×10⁻⁷
0
0
40
80
120
T*2


BACKGROUND (SEP 24)
11:29 10-NOV-86
HEAT CAPACITY
2.5×10⁻⁵
2×10⁻⁵
1.5×10⁻⁵
1×10⁻⁵
5×10⁻⁶
0
4
6
8
10
12
14
TEMPERATURE

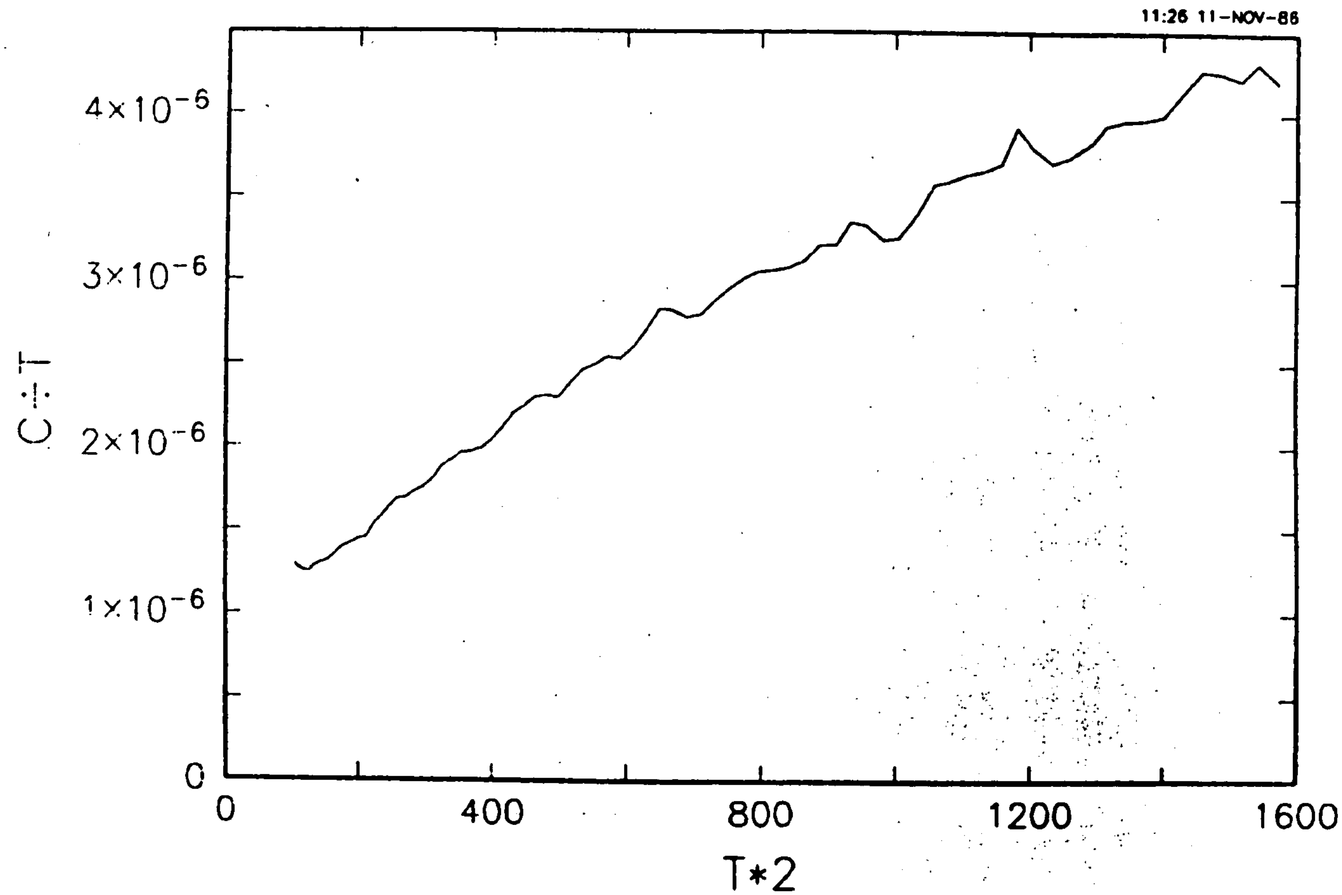
BACKGROUND (NOV4)




BACKGROUND (SEP 24)
13:31 10-NOV-86
8×10⁻⁷
6×10⁻⁷
4×10⁻⁷
2×10⁻⁷
0
C÷T
0
20
40
60
T*2


BACKGROUND (OCT 22)
11:43 11-NOV-86
8×10^{-7}
6×10^{-7}
4×10^{-7}
2×10^{-7}
0
C ÷ T
0
20
40
60
80
100
T*2

BACKGROUND (OCT 22)



Title: RUO2 VS TEMP PROGRAM
Run Id. - NO76LTCA.DAT
Time and Date: 07:35:26 11-03-1986 - 08:11:58 11-~~03~~ 07-1986
Parameter lines = 13
Min Temp to Plot = 1.500 K
Max Temp to Plot = 12.50 K
Min Volts to Plot = 8.30 Volts
Max Volts to Plot = 10.5 Volts
Plot Title = RUO2 VS TEMP
X Axis Plot Label = Sample Temp (K)
Y Axis Plot Label = RUO2 (Volts)
Start Temperature = 002 K
Temperature Step = 0.5 K
Temperature Stop = 010 K
LR400 Range = 20000 Ohms
Temperature Dev. = 0.050 K
Wait Time = 0010 seconds
Notebook messages = 4
RUO2 Calibration vs C2329 Carbon Glass Resistor
4 WIRE CONFIGURATION FOR BOLOMETER
TEMP. CALIBRATION 2-12K
STEPPING UP
Number of points = 15 Values per point = 4

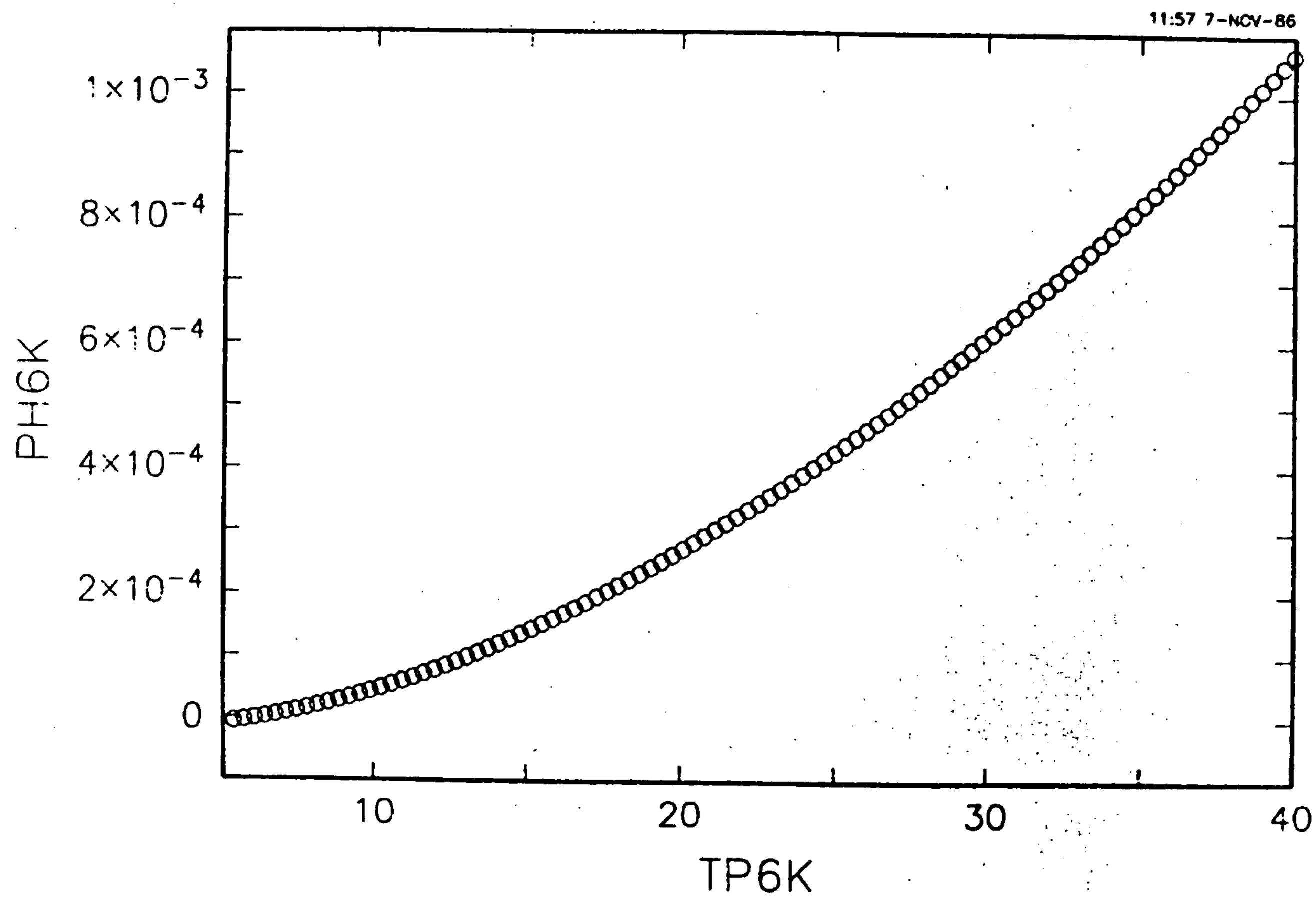
RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
10.18E+00	19.85E-01	20.00E-01	0.050
98.68E-01	24.86E-01	25.00E-01	0.050
96.38E-01	29.87E-01	30.00E-01	0.050
94.60E-01	34.94E-01	35.00E-01	0.050
93.29E-01	39.99E-01	40.00E-01	0.050
92.07E-01	45.01E-01	45.00E-01	0.050
91.02E-01	49.97E-01	50.00E-01	0.050
90.20E-01	54.65E-01	55.00E-01	0.050
89.37E-01	60.15E-01	60.00E-01	0.050
88.69E-01	65.33E-01	65.00E-01	0.050
88.09E-01	70.19E-01	70.00E-01	0.050
87.54E-01	75.08E-01	75.00E-01	0.050
87.04E-01	80.30E-01	80.00E-01	0.050
86.60E-01	85.18E-01	85.00E-01	0.050
86.12E-01	90.30E-01	90.00E-01	0.050

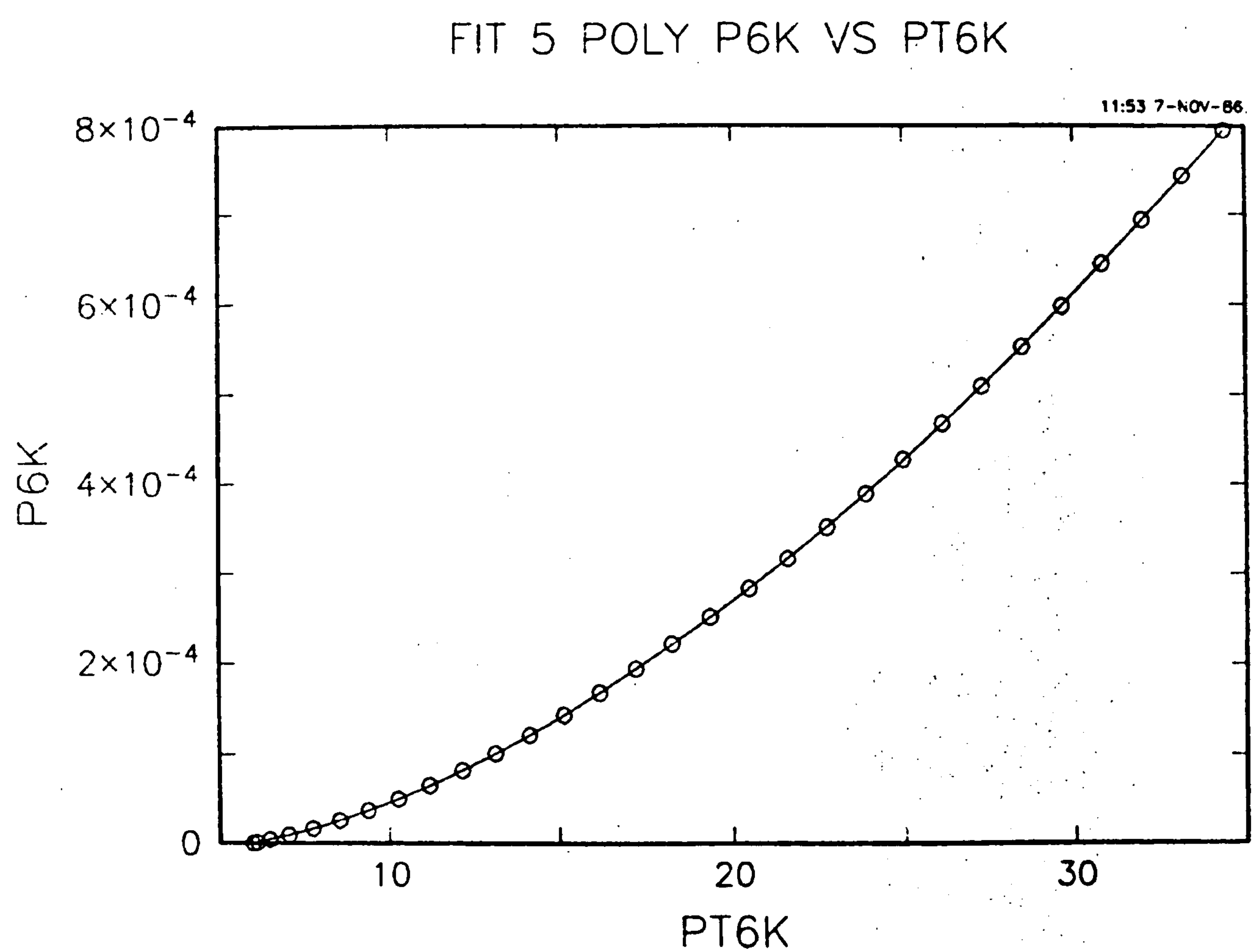
Title: RUO2 VS TEMP PROGRAM
Run Id. - NO66HTCA.DAT
Time and Date: 07:56:24 11-02-1986 - 10:29:36 11-~~02~~06-1986
Parameter lines = 13
Min Temp to Plot = 05.00 K
Max Temp to Plot = 40.00 K
Min Volts to Plot = 7.50 Volts
Max Volts to Plot = 9.10 Volts
Plot Title = RUO2 VS TEMP
X Axis Plot Label = Sample Temp (K)
Y Axis Plot Label = RUO2 (Volts)
Start Temperature = 5.0 K
Temperature Step = 1.0 K
Temperature Stop = 040 K
LR400 Range = 02000 Ohms
Temperature Dev. = 0.100 K
Wait Time = 0012 seconds
Notebook messages = 4
RUO2 Calibration vs C2329 Carbon Glass Resistor
4 WIRE CONFIGURATION FOR BOLOMETER
TEMP. CALIBRATION 5-40K
STEPPING UP
Number of points = 26 Values per point = 4

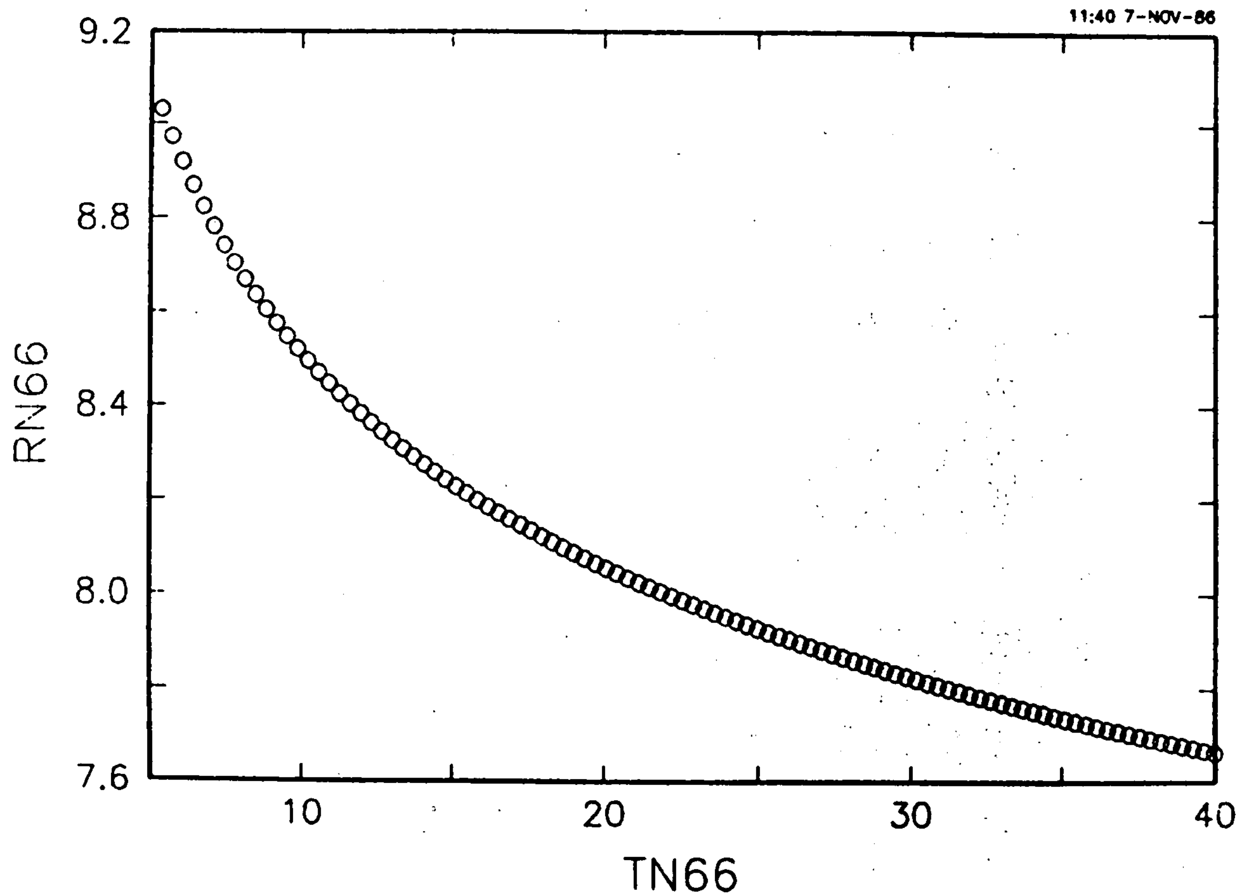
RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
91.04E-01	49.67E-01	50.00E-01	0.100
89.37E-01	59.54E-01	60.00E-01	0.100
88.03E-01	69.63E-01	70.00E-01	0.100
86.85E-01	79.56E-01	80.00E-01	0.100
85.95E-01	89.48E-01	90.00E-01	0.100
85.17E-01	99.64E-01	10.00E+00	0.100
84.49E-01	10.96E+00	11.00E+00	0.100
83.87E-01	12.00E+00	12.00E+00	0.100
83.33E-01	12.99E+00	13.00E+00	0.100
82.84E-01	13.98E+00	14.00E+00	0.100
82.38E-01	14.98E+00	15.00E+00	0.100
81.96E-01	15.99E+00	16.00E+00	0.100
81.56E-01	17.00E+00	17.00E+00	0.100
81.20E-01	18.00E+00	18.00E+00	0.100
80.87E-01	19.03E+00	19.00E+00	0.100
80.57E-01	19.96E+00	20.00E+00	0.100
80.28E-01	20.96E+00	21.00E+00	0.100
80.02E-01	21.99E+00	22.00E+00	0.100
79.75E-01	23.00E+00	23.00E+00	0.100
79.50E-01	23.96E+00	24.00E+00	0.100
79.27E-01	24.99E+00	25.00E+00	0.100
79.04E-01	25.93E+00	26.00E+00	0.100
78.82E-01	26.99E+00	27.00E+00	0.100
78.62E-01	28.07E+00	28.00E+00	0.100
78.41E-01	28.94E+00	29.00E+00	0.100
78.22E-01	30.02E+00	30.00E+00	0.100

Title: RUO2 VS TEMP PROGRAM
Run Id. - NO66HTCB.DAT
Time and Date: 10:37:35 11-02-1986 - 11:24:09 11-~~02~~ 06-1986
Parameter lines = 13
Min Temp to Plot = 25.00 K
Max Temp to Plot = 40.00 K
Min Volts to Plot = 7.50 Volts
Max Volts to Plot = 7.95 Volts
Plot Title = RUO2 VS TEMP
X Axis Plot Label = Sample Temp (K)
Y Axis Plot Label = RUO2 (Volts)
Start Temperature = 026 K
Temperature Step = 1.0 K
Temperature Stop = 040 K
LR400 Range = 02000 Ohms
Temperature Dev. = 0.200 K
Wait Time = 0012 seconds
Notebook messages = 4
RUO2 Calibration vs C2329 Carbon Glass Resistor
4 WIRE CONFIGURATION FOR BOLOMETER
TEMP. CALIBRATION 26-40K
STEPPING UP
Number of points = 14 Values per point = 4

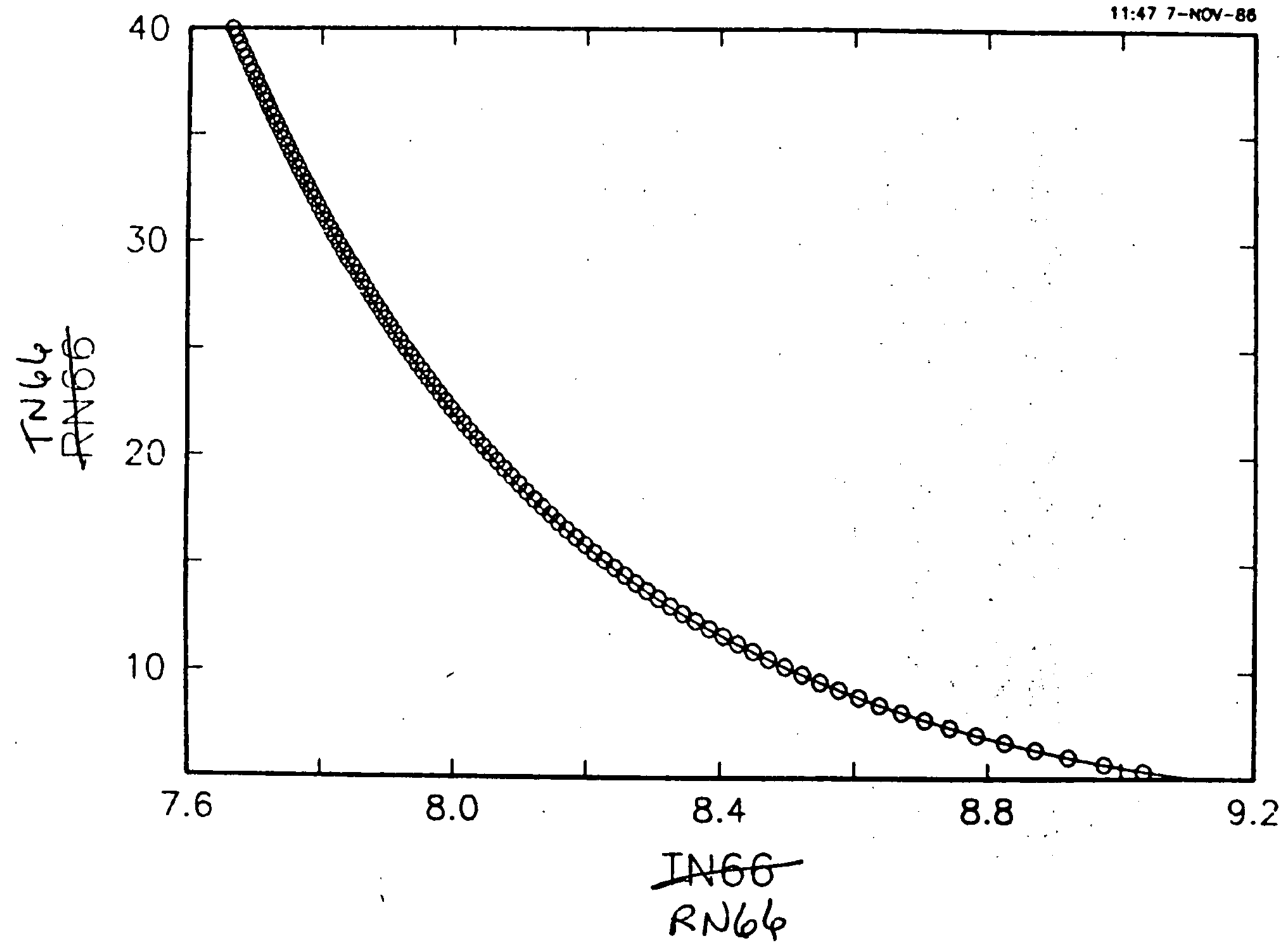
RUO2 VOLTS	C2329 TEMP	SET TEMP	TEMP DEV
79.08E-01	25.82E+00	26.00E+00	0.200
78.87E-01	27.13E+00	27.00E+00	0.200
78.64E-01	28.18E+00	28.00E+00	0.200
78.44E-01	29.09E+00	29.00E+00	0.200
78.25E-01	30.13E+00	30.00E+00	0.200
78.06E-01	31.14E+00	31.00E+00	0.200
77.88E-01	32.13E+00	32.00E+00	0.200
77.72E-01	33.03E+00	33.00E+00	0.200
77.55E-01	33.96E+00	34.00E+00	0.200
77.39E-01	35.02E+00	35.00E+00	0.200
77.22E-01	36.09E+00	36.00E+00	0.200
77.06E-01	37.03E+00	37.00E+00	0.200
76.91E-01	38.06E+00	38.00E+00	0.200
76.75E-01	39.15E+00	39.00E+00	0.200


11:57 7-NOV-86
1×10^{-3}
8×10^{-4}
6×10^{-4}
4×10^{-4}
2×10^{-4}
0
PH6K
10
20
30
40
TP6K

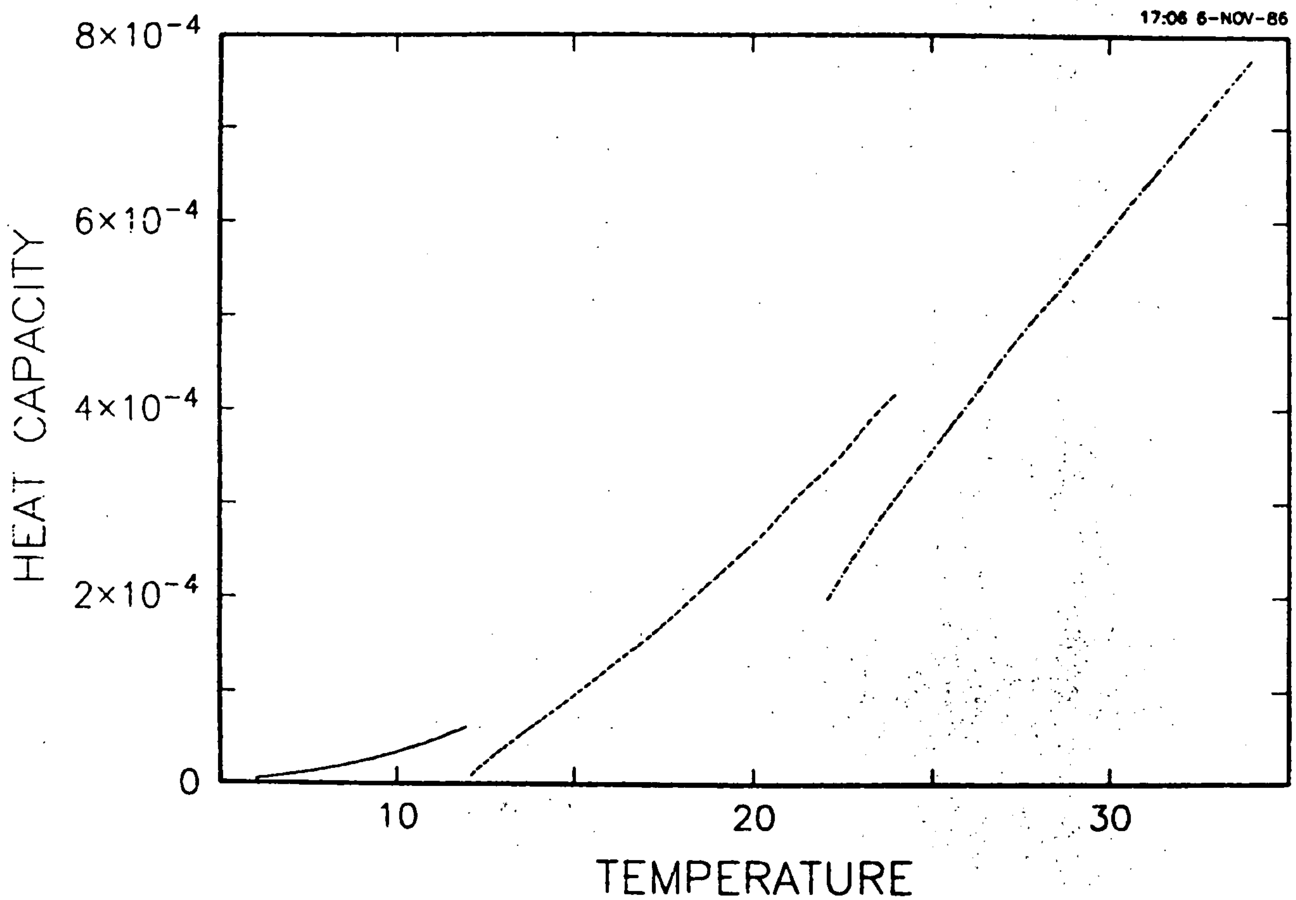

FIT 5 POLY P6K VS PT6K
11:53 7-NOV-86
P6K
8×10^{-4}
6×10^{-4}
4×10^{-4}
2×10^{-4}
0
10
20
30
PT6K


11:40 7-NOV-86
9.2
8.8
8.4
8.0
7.6
RN66
10
20
30
40
TN66

FIT 5 POLY RN66 AND TN66

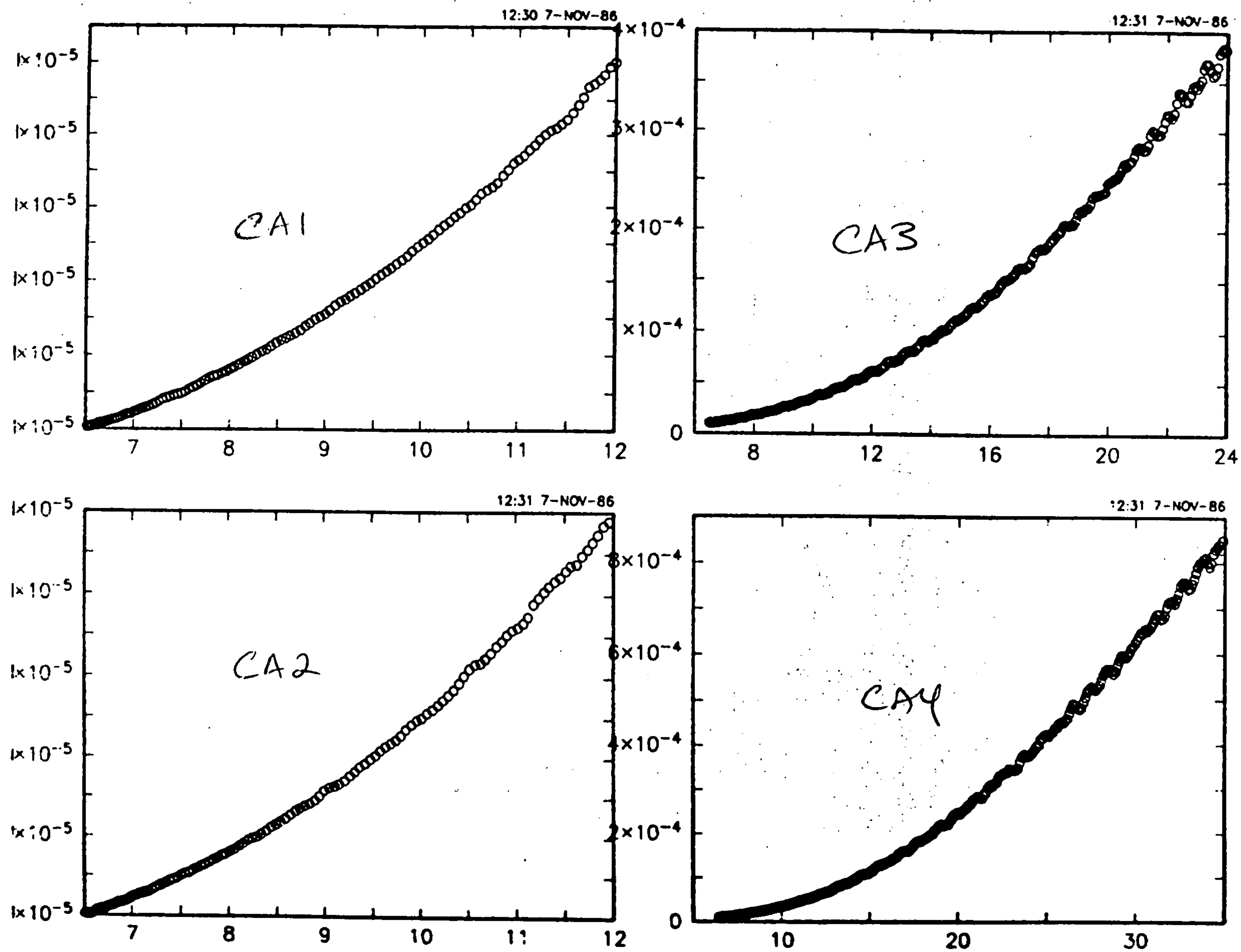


ZURICH OXIDE — BLCO 21-II

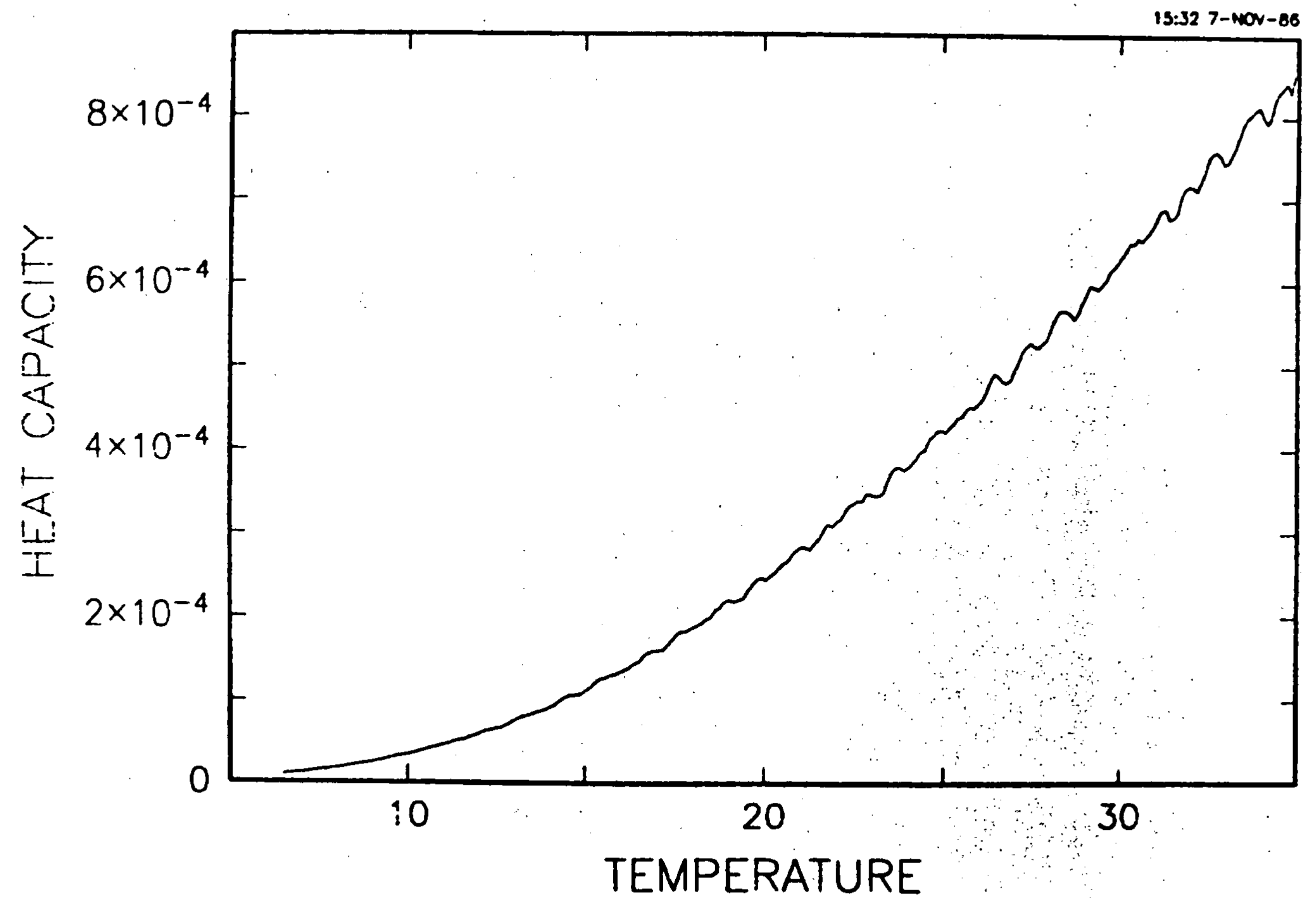


Heat (

Zurich oxide



CA5 VS TA5 WITH CA4 VS TA4

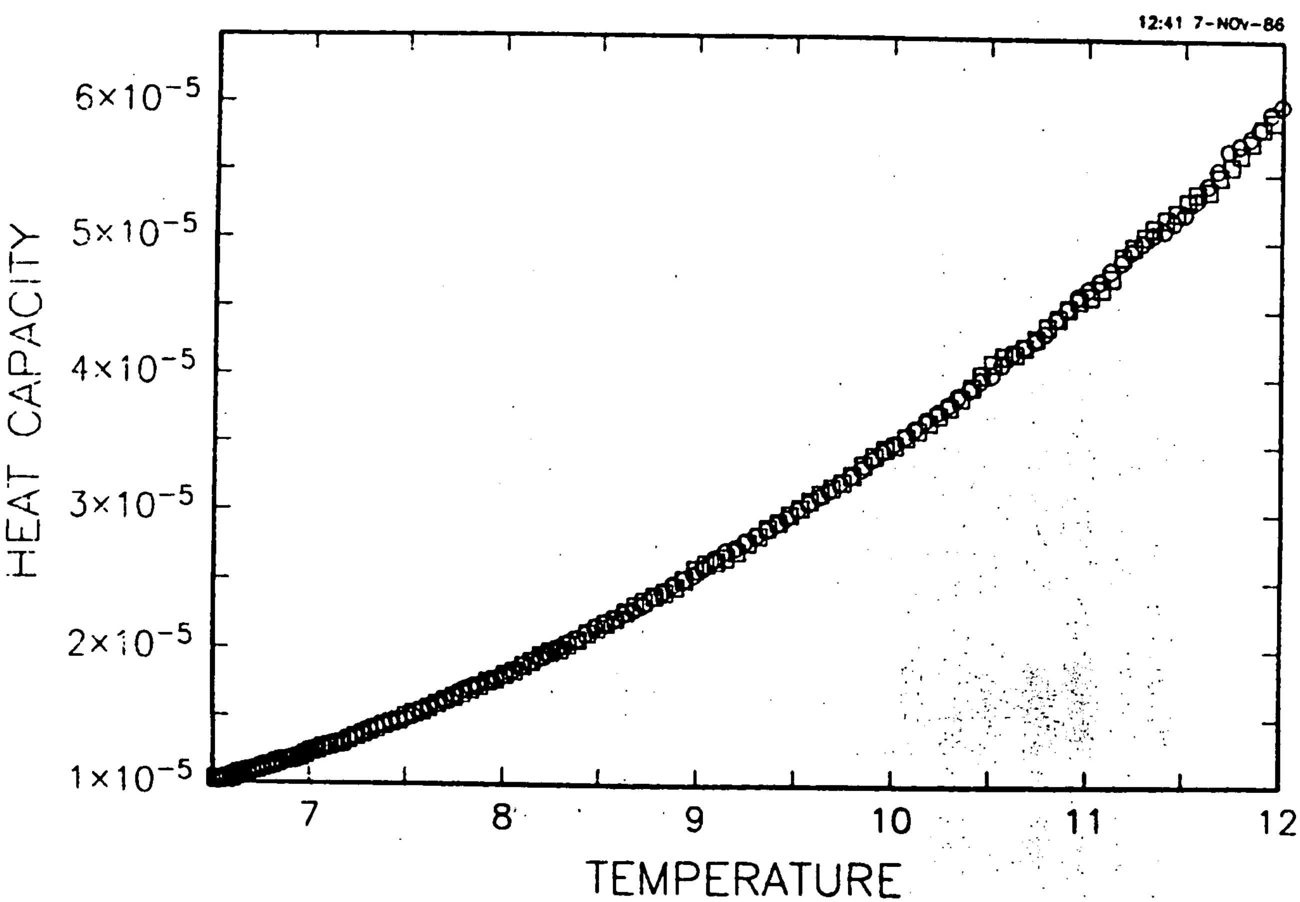


TA4 = 100 pt in R vs T fit

TA5 = 1000 pts in R vs T fit

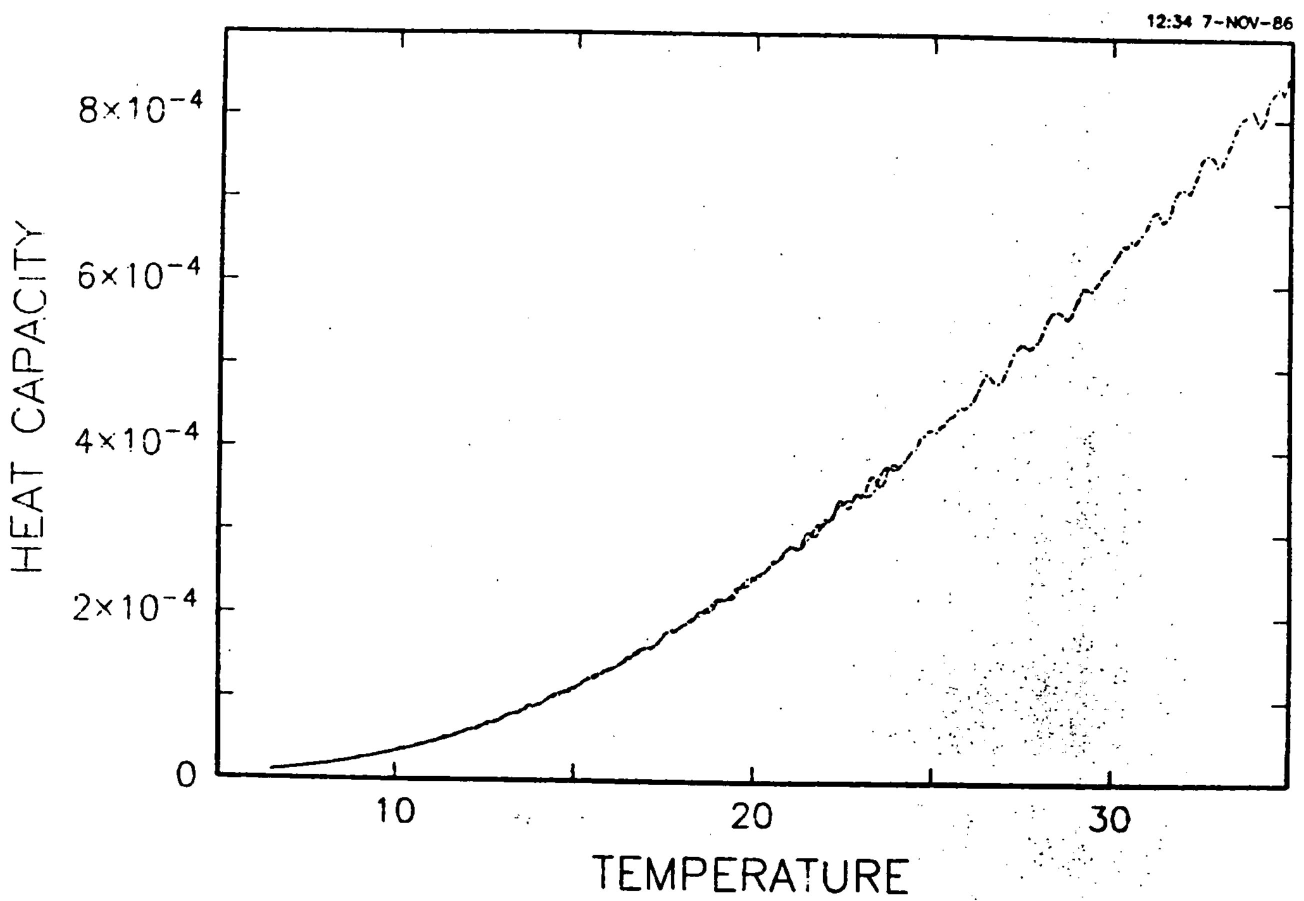
$\Rightarrow$ no diff.

CA1 VS TA1 WITH CA2 VS TA2

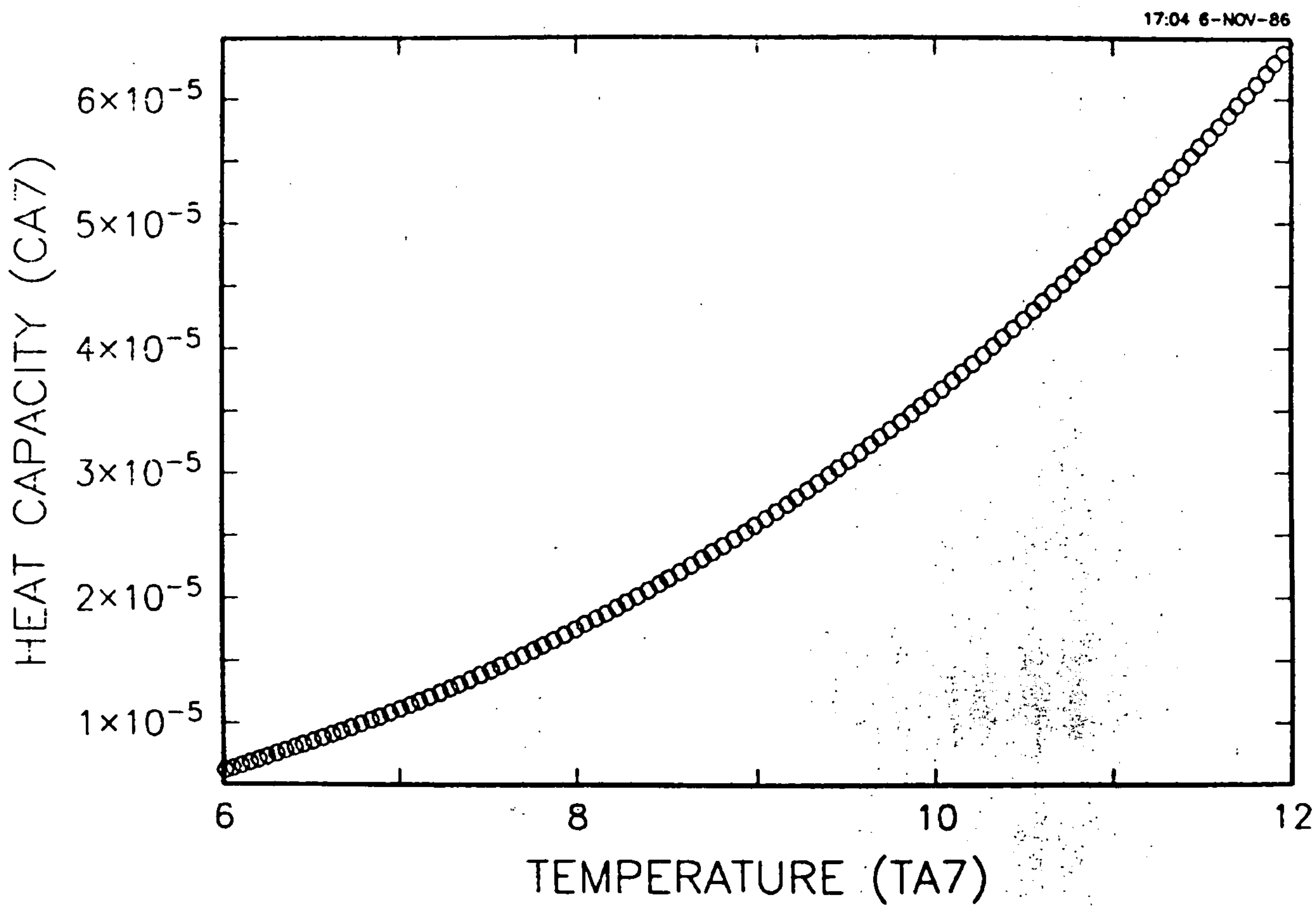


Zurich Oxide

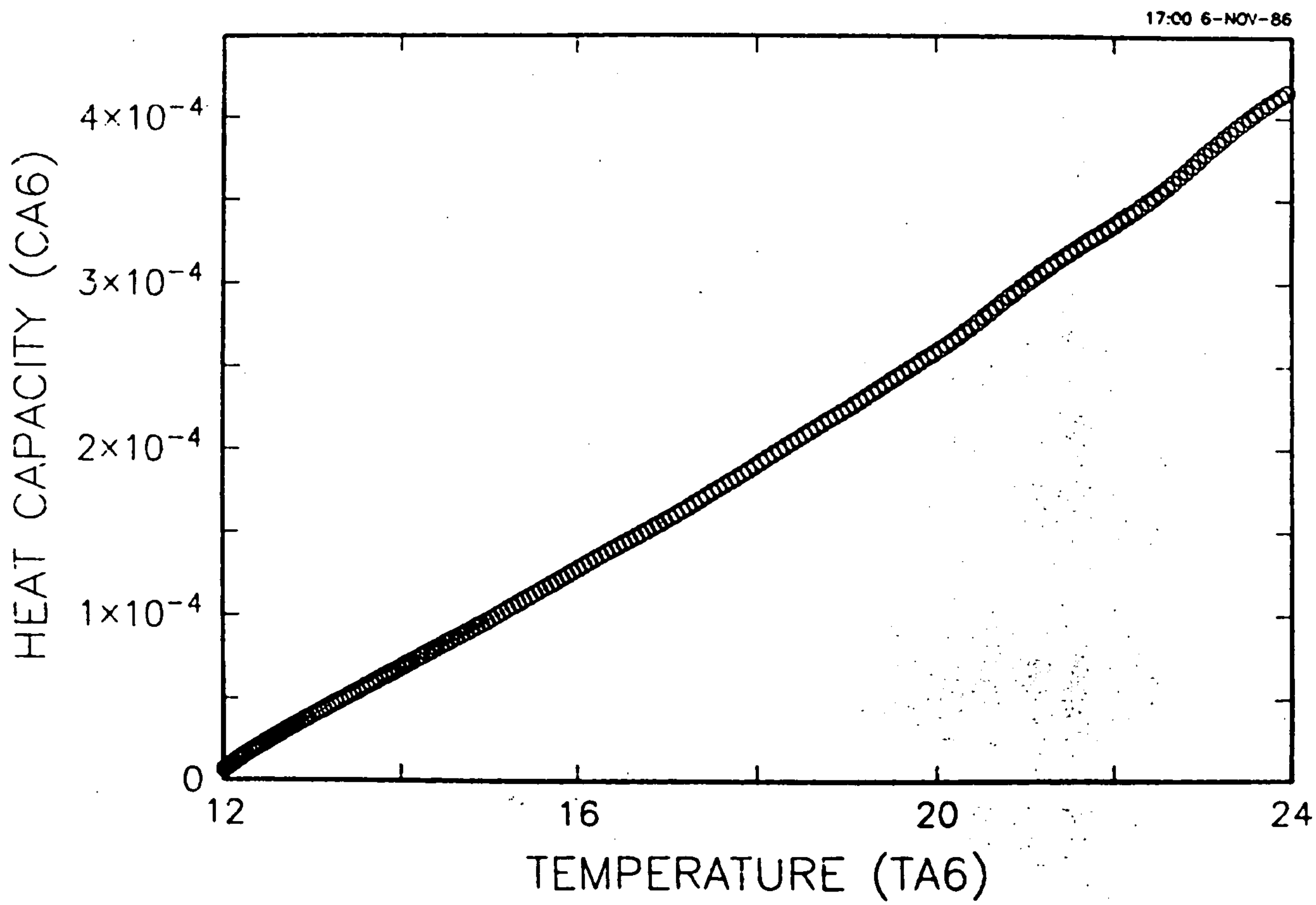
CA1 VS TA1 WITH CA3 VS TA3 WITH CA4 VS TA4



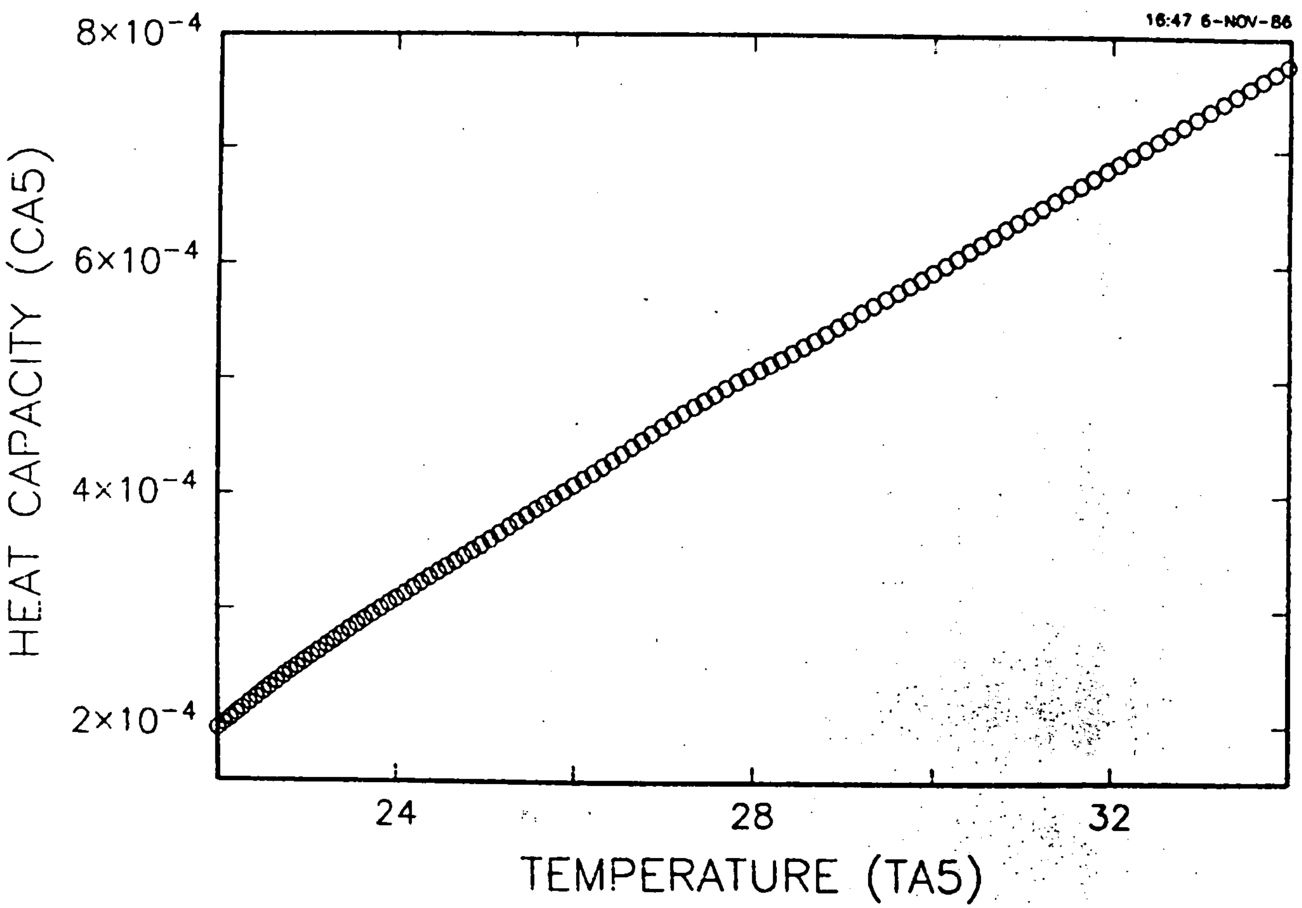
ZURICH OXIDE



ZURICH OXIDE

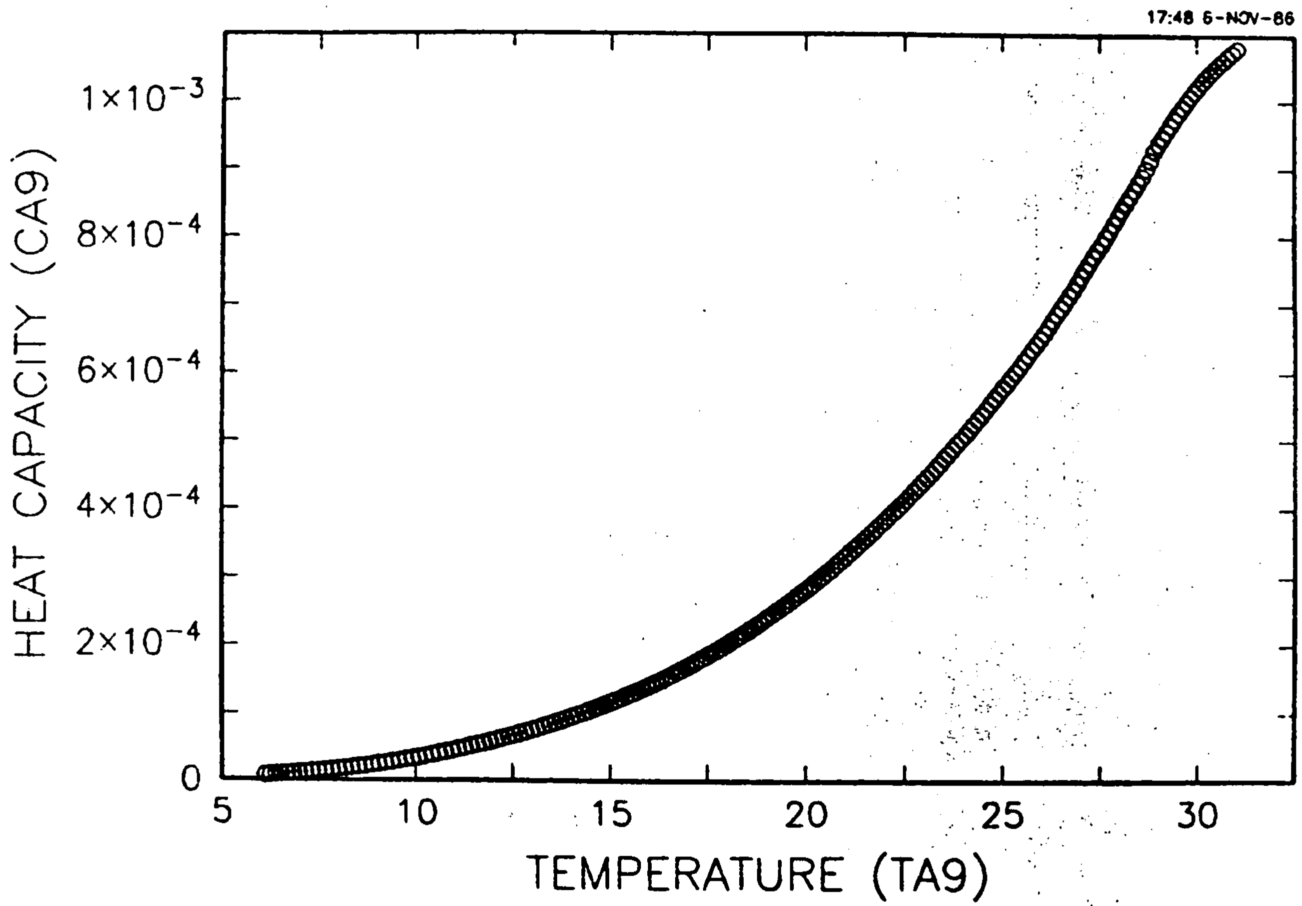


ZURICH OXIDE



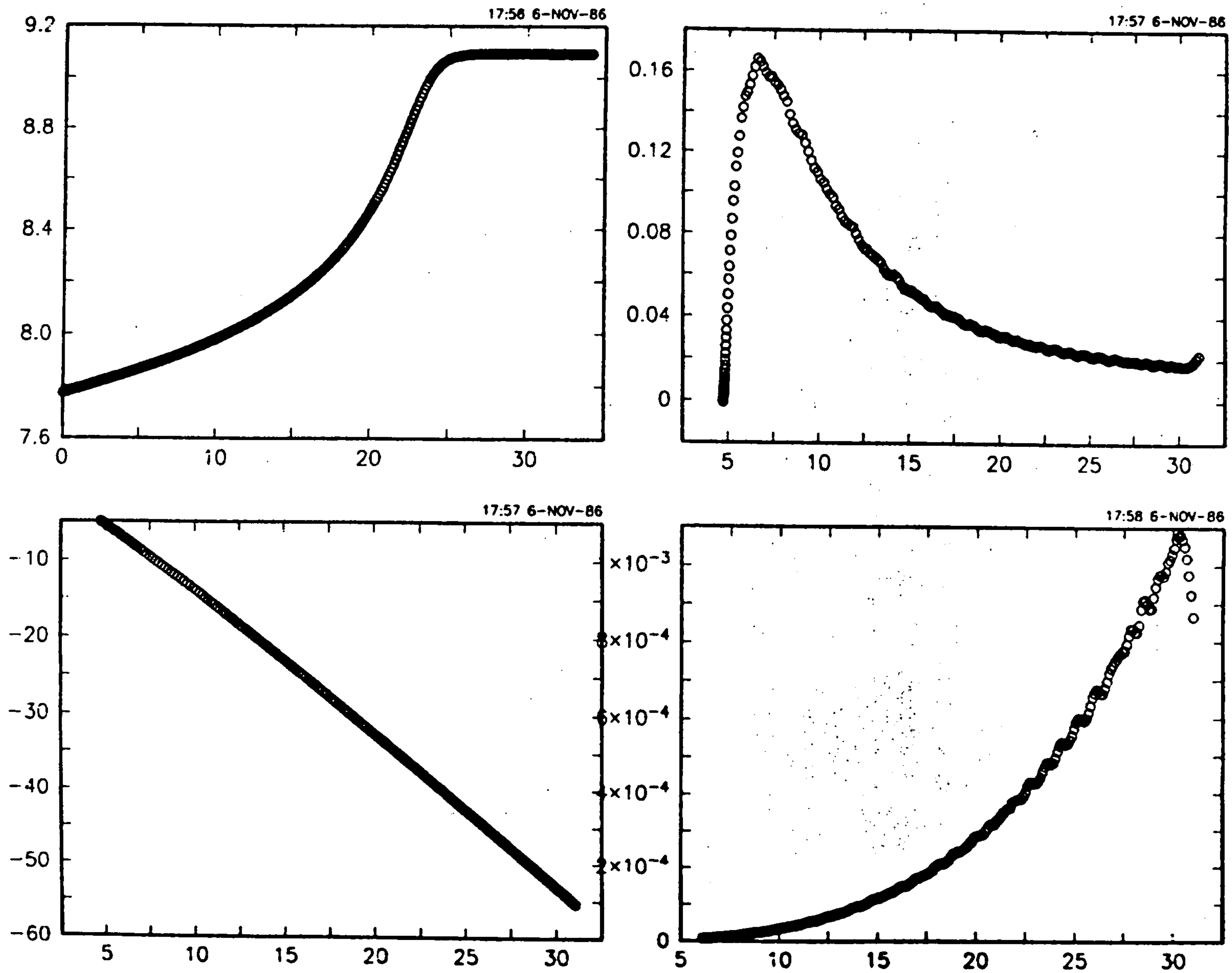
NΦ6670HE

ZURICH OXIDE

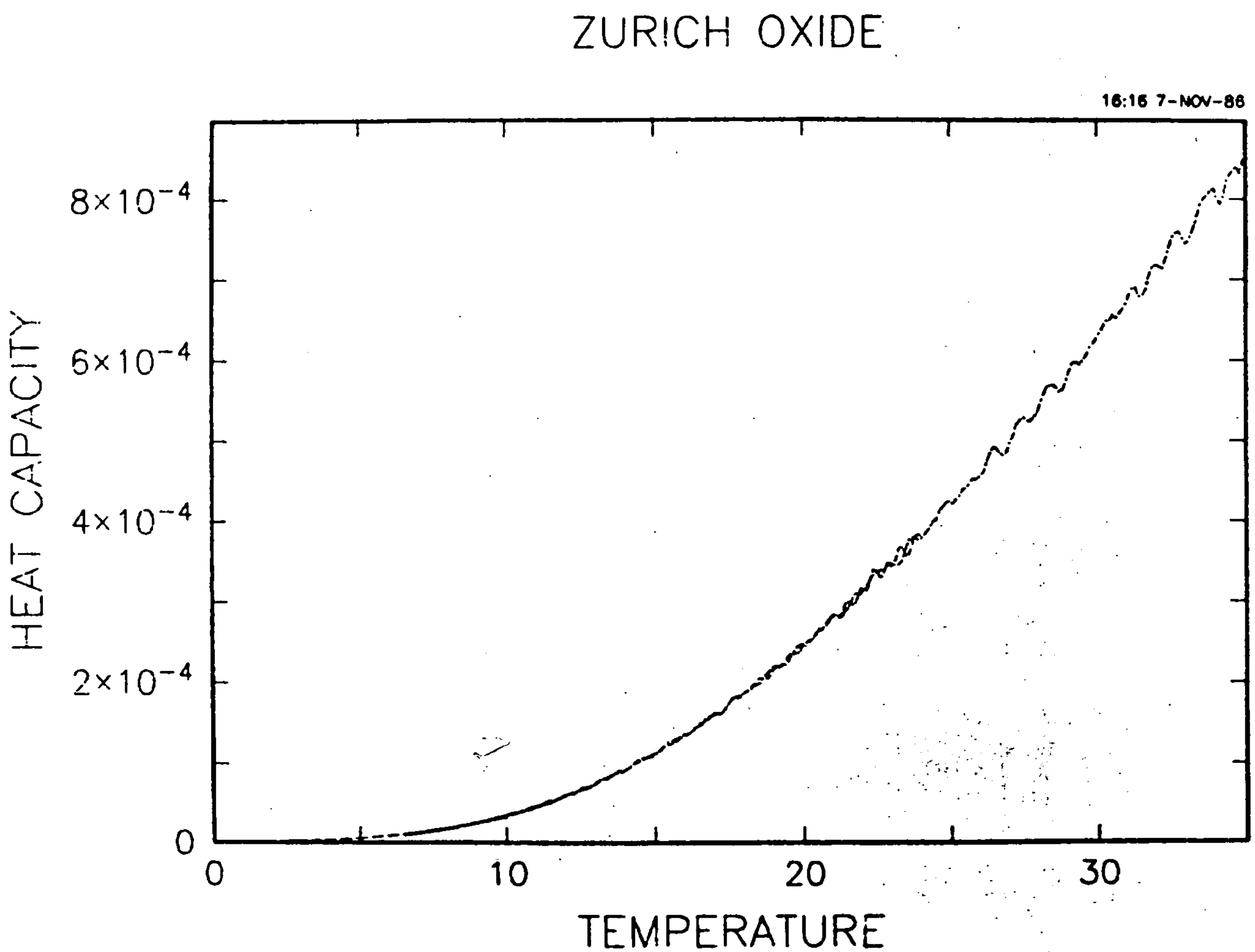


AA←20
FN9

Zurich Oxide NΦ66ZoHE



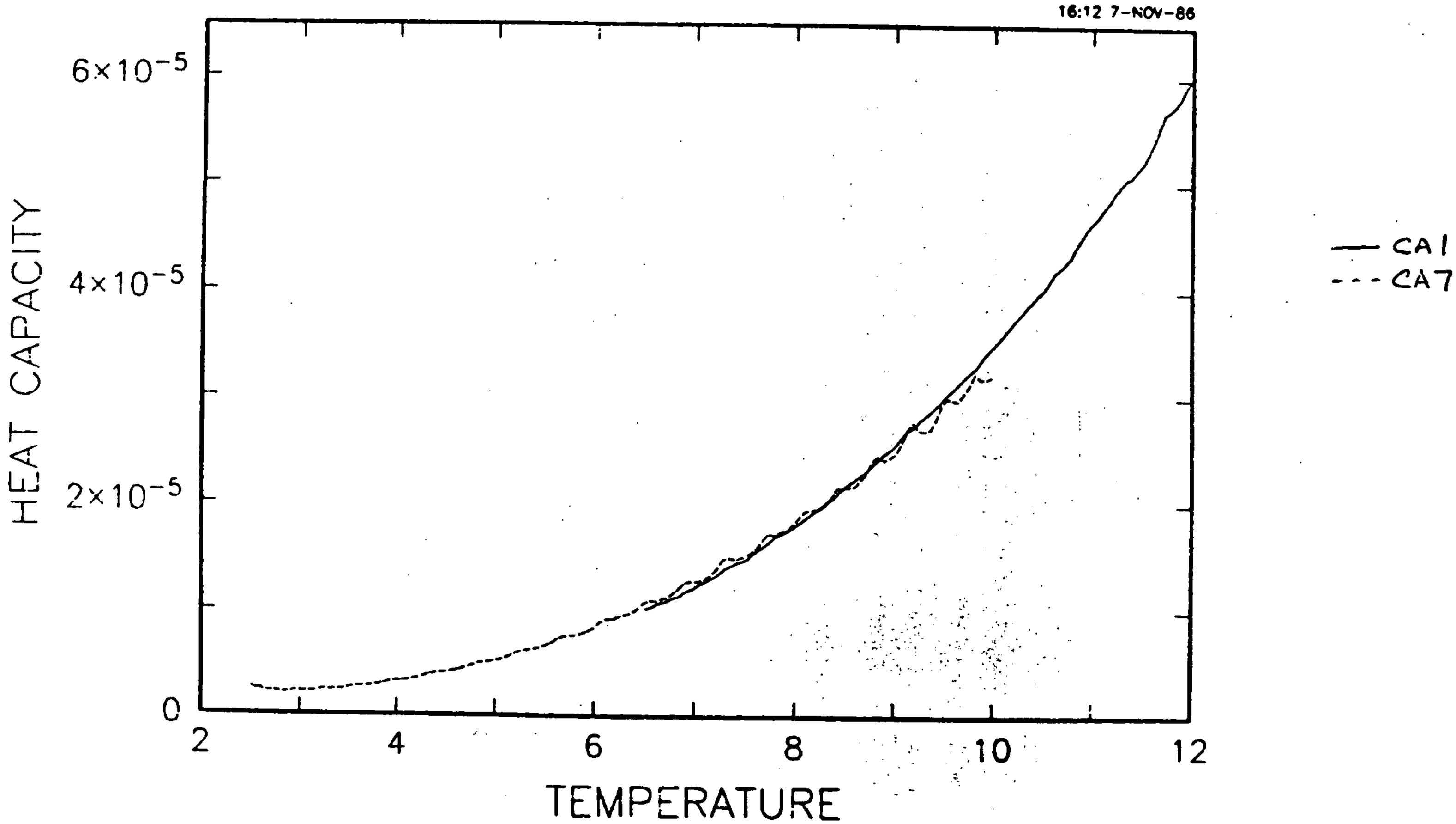
ΛA = 4



3 RUNS 6 Nov
Superposed

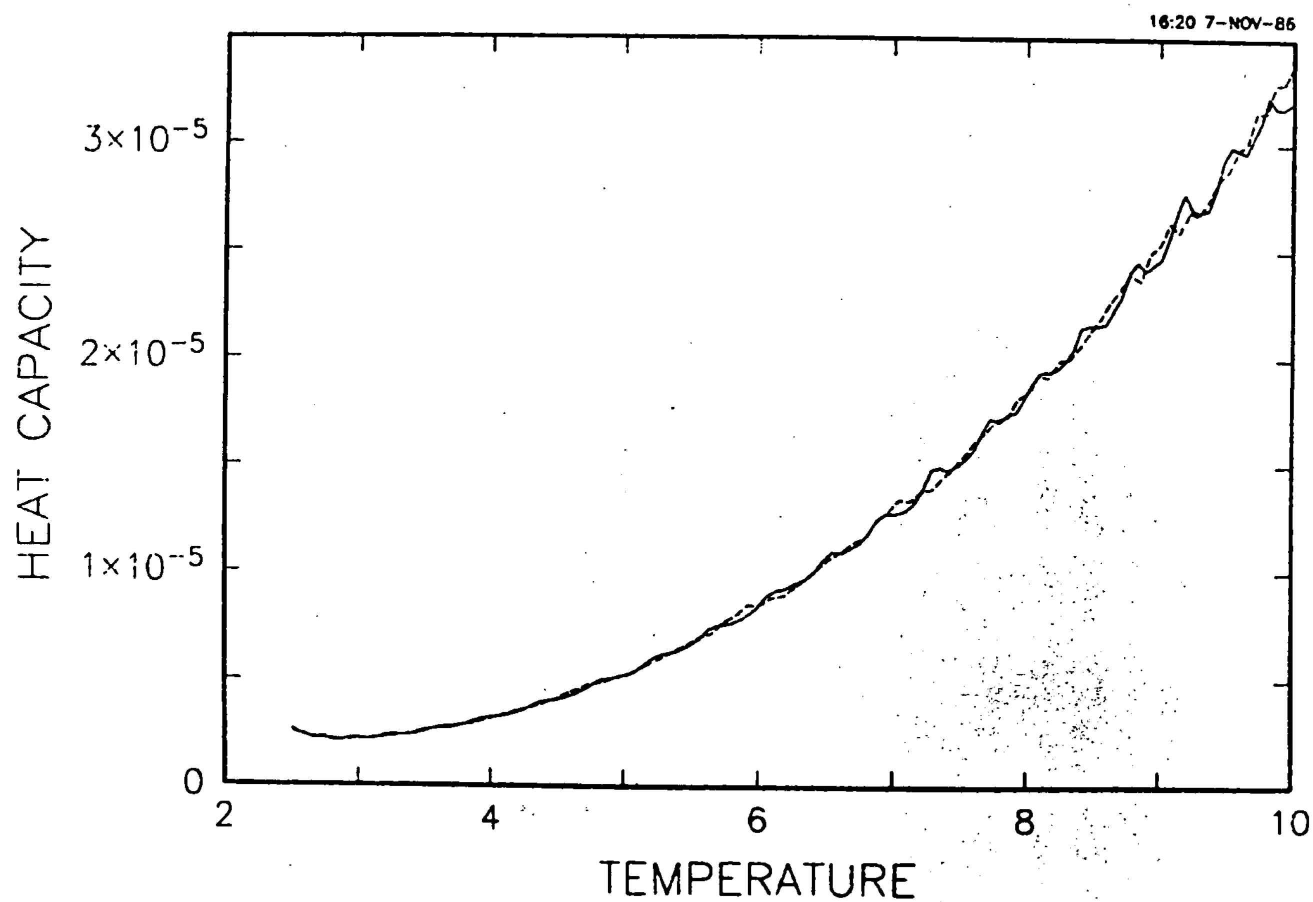
6-12K
6-25K
6-35K

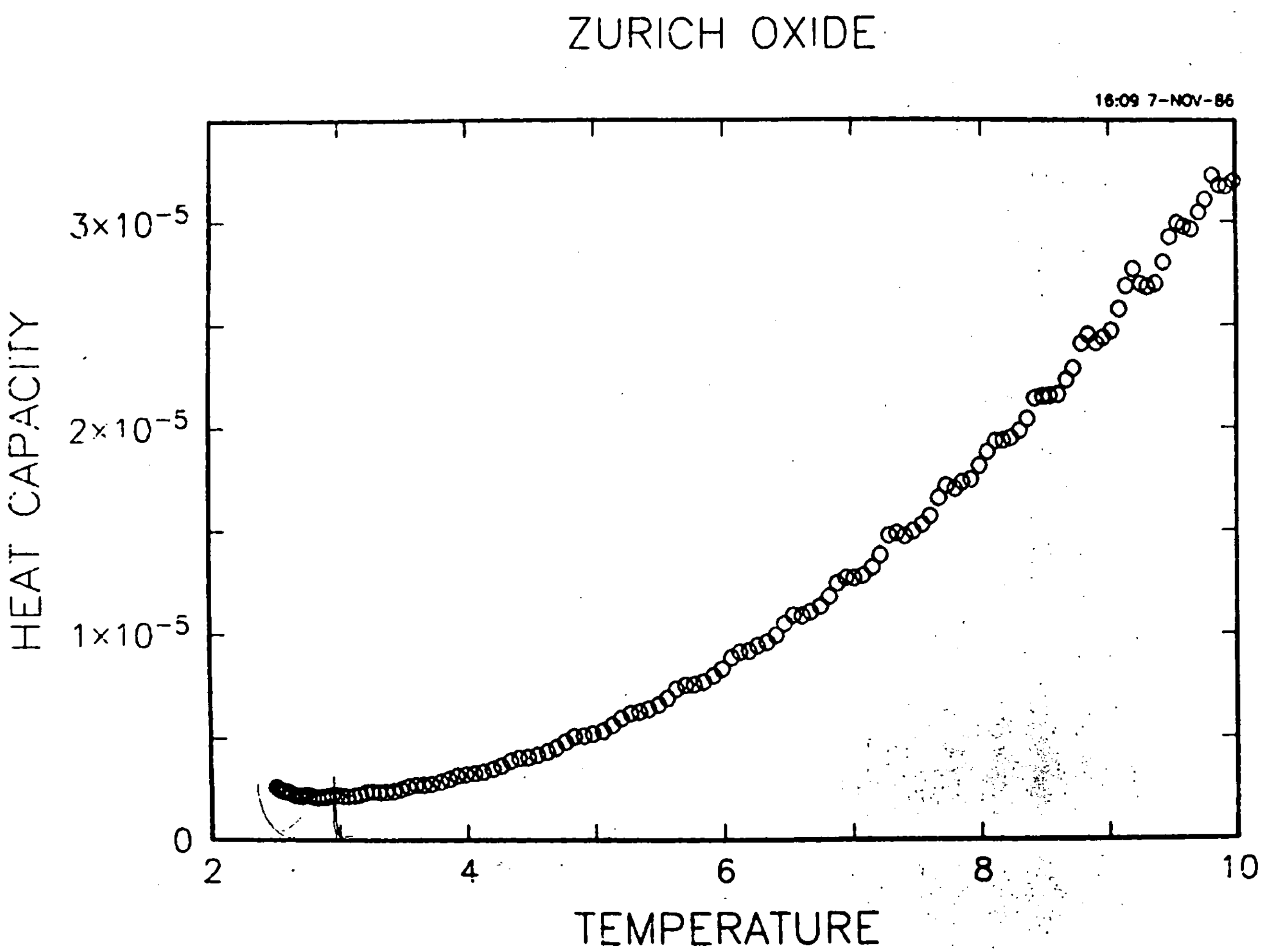
ZURICH OXIDE



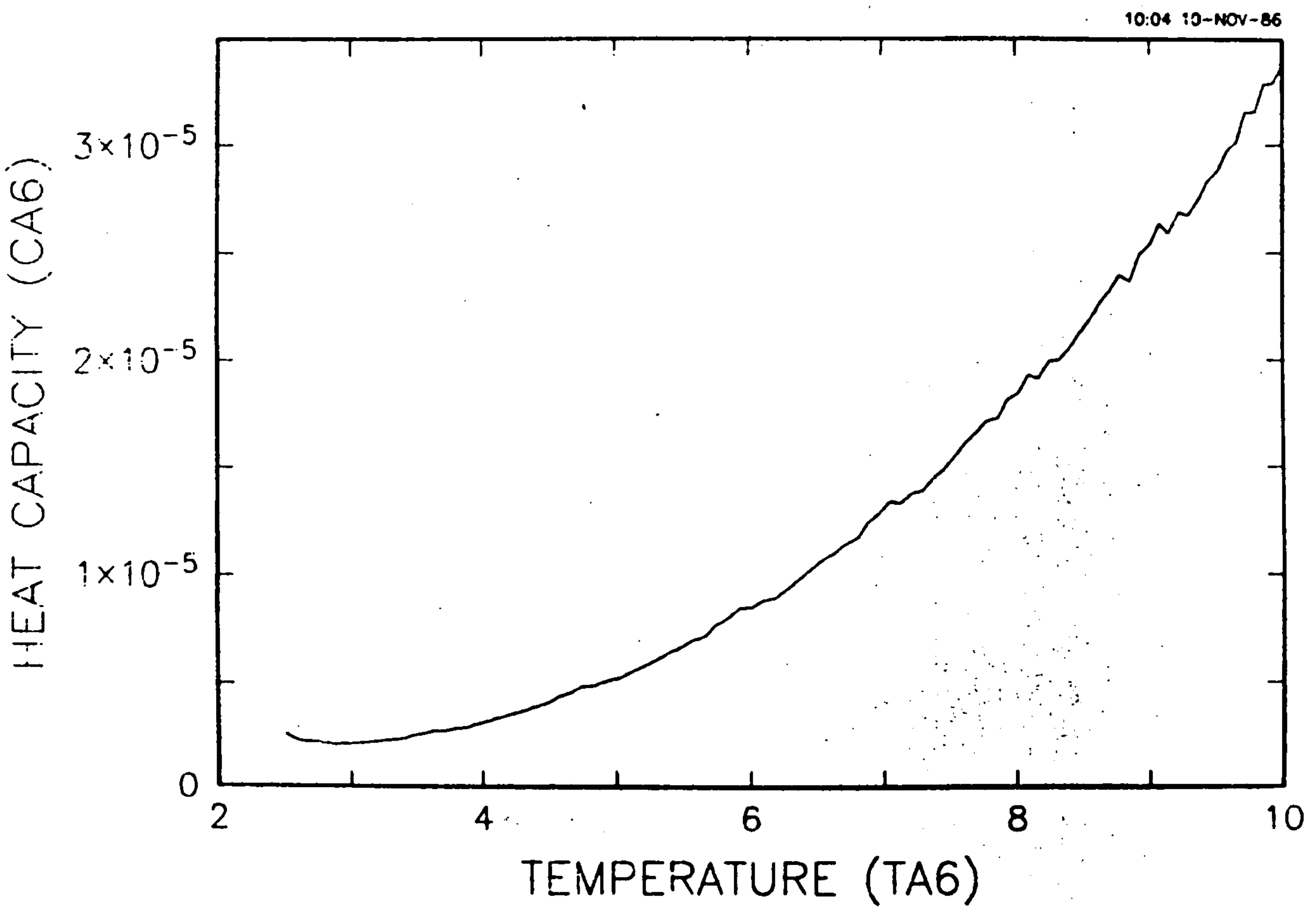
NΦ7620LA.~~DAT~~
compared to
NΦ7620LB.~~DAT~~ essentially the same

ZURICH OXIDE

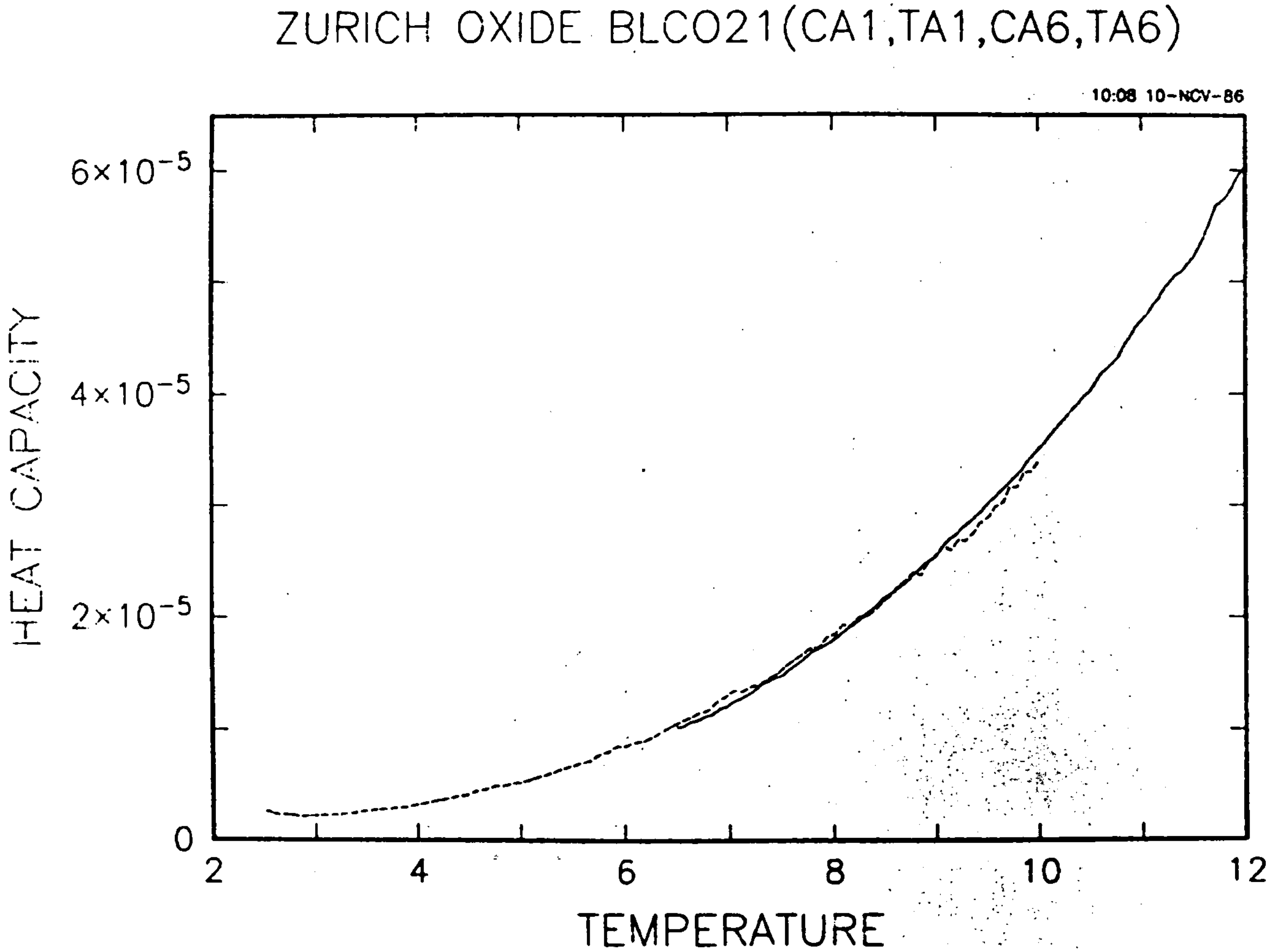



ZURICH OXIDE
16:09 7-NOV-86
HEAT CAPACITY
3×10⁻⁵
2×10⁻⁵
1×10⁻⁵
0
2
4
6
8
10
TEMPERATURE

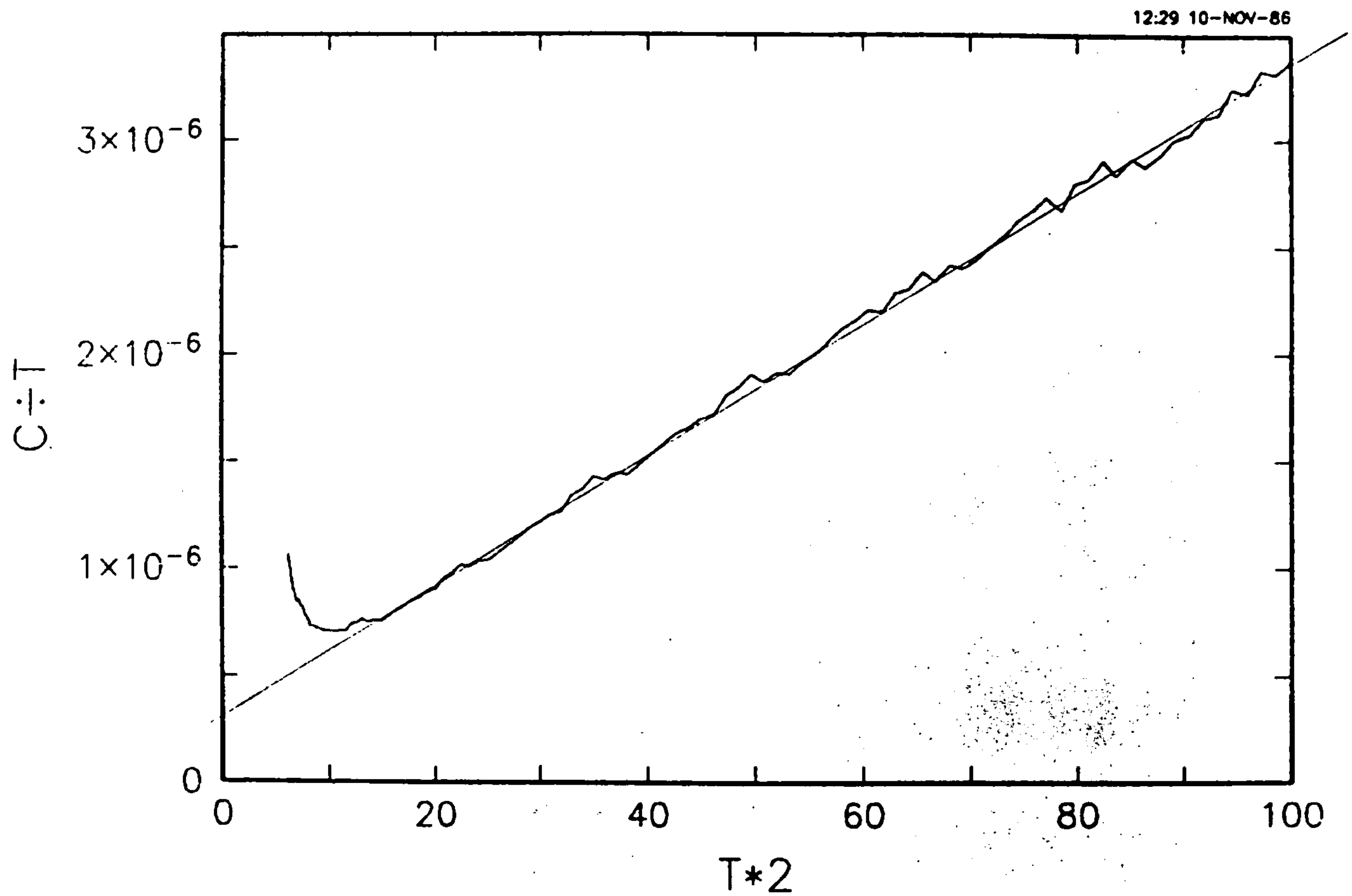
ZURICH OXIDE BLCO21



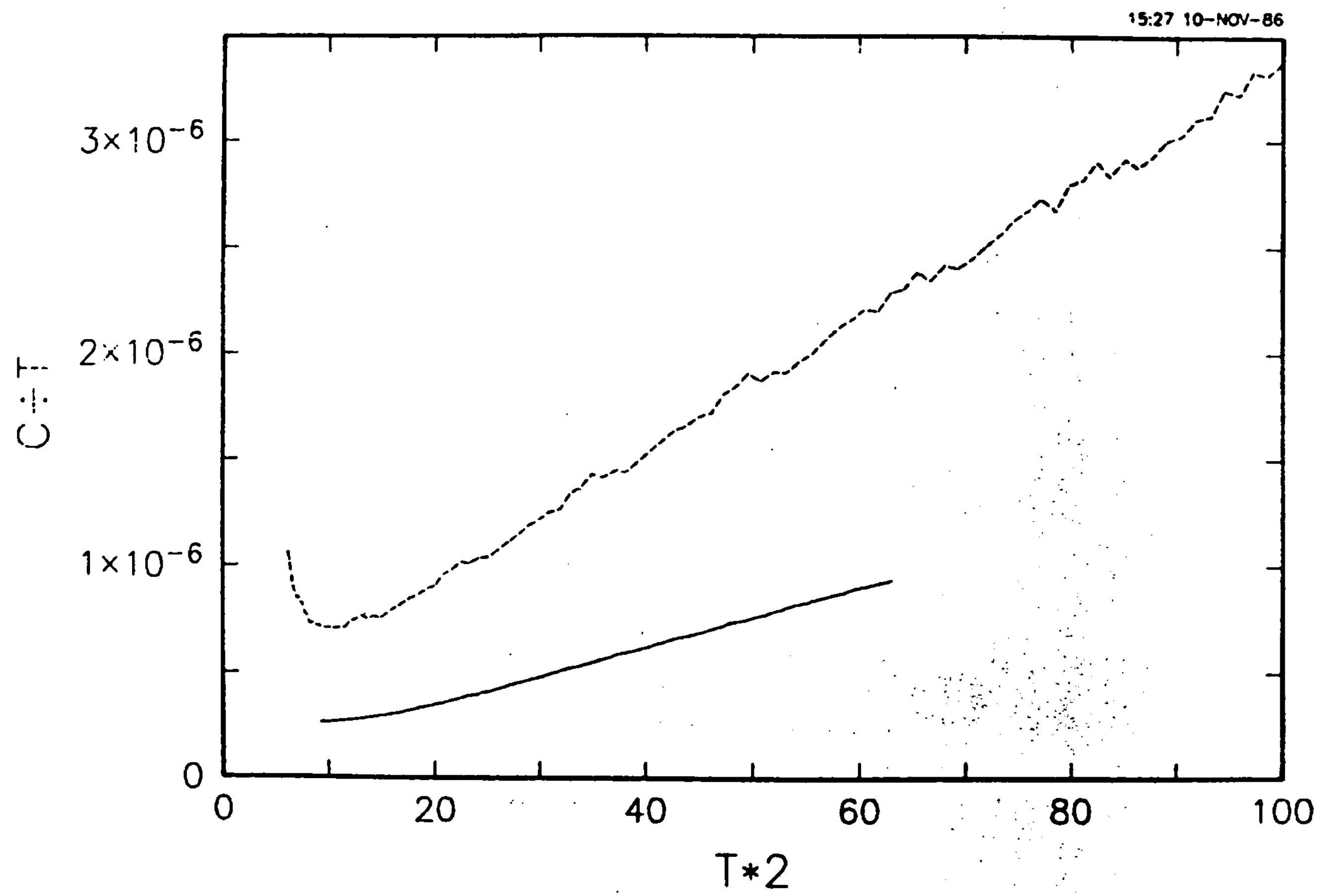
Check of overlap of data
2-10 K
6-12 K



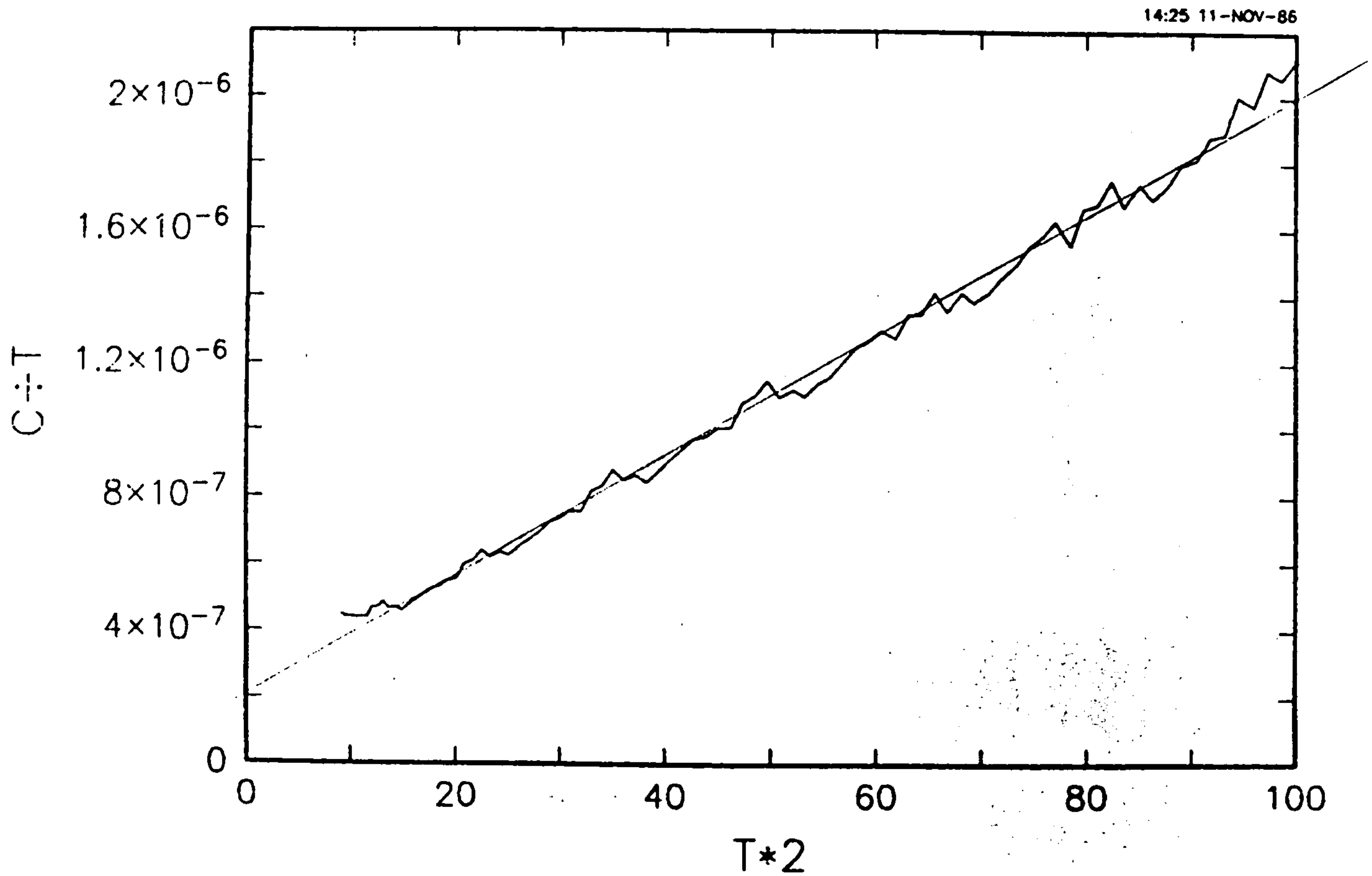
ZURICH OXIDE BLCO21 + BackGrd



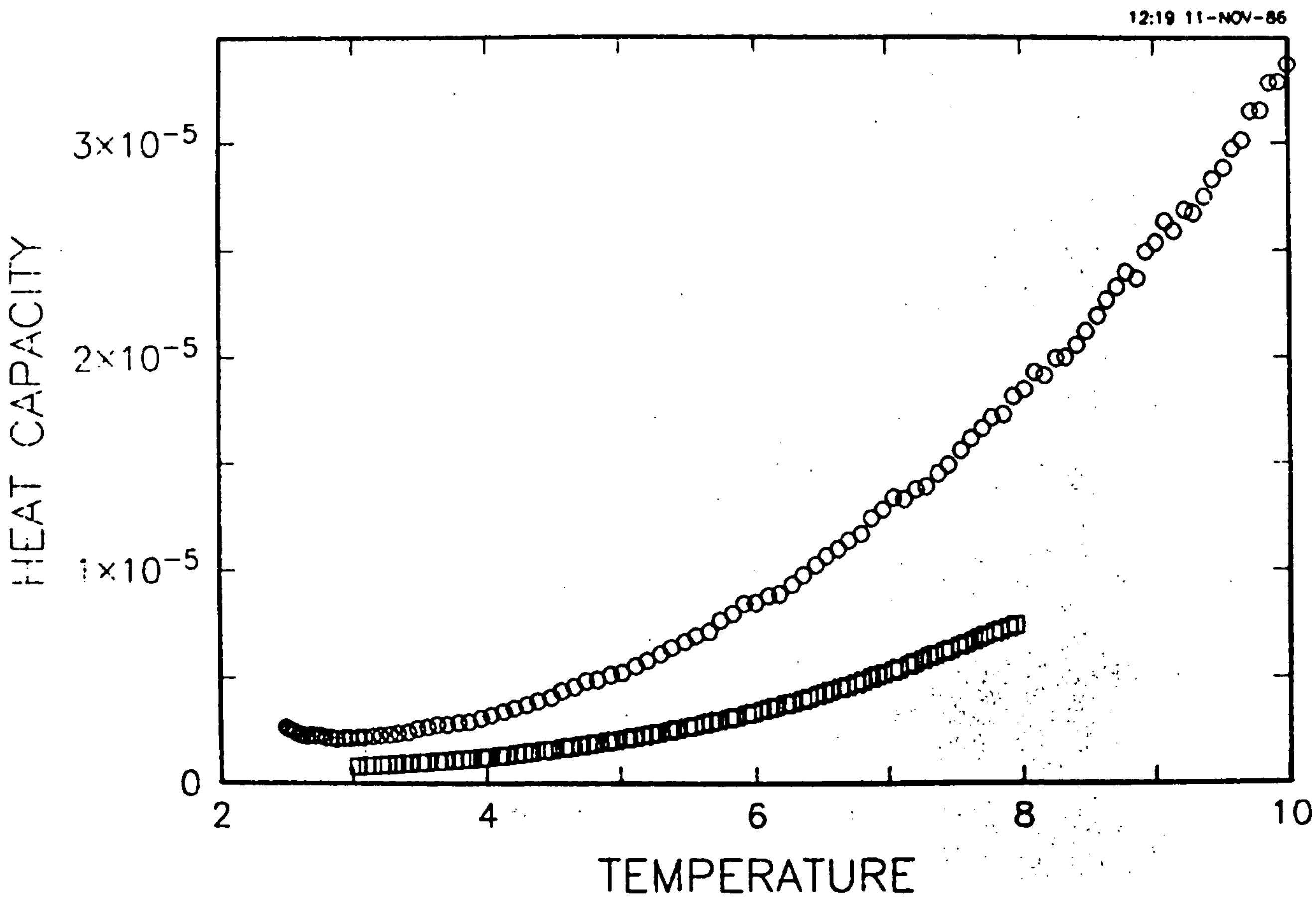
(ZURICH OXIDE+BACKGROUND) AND BACKGROUND



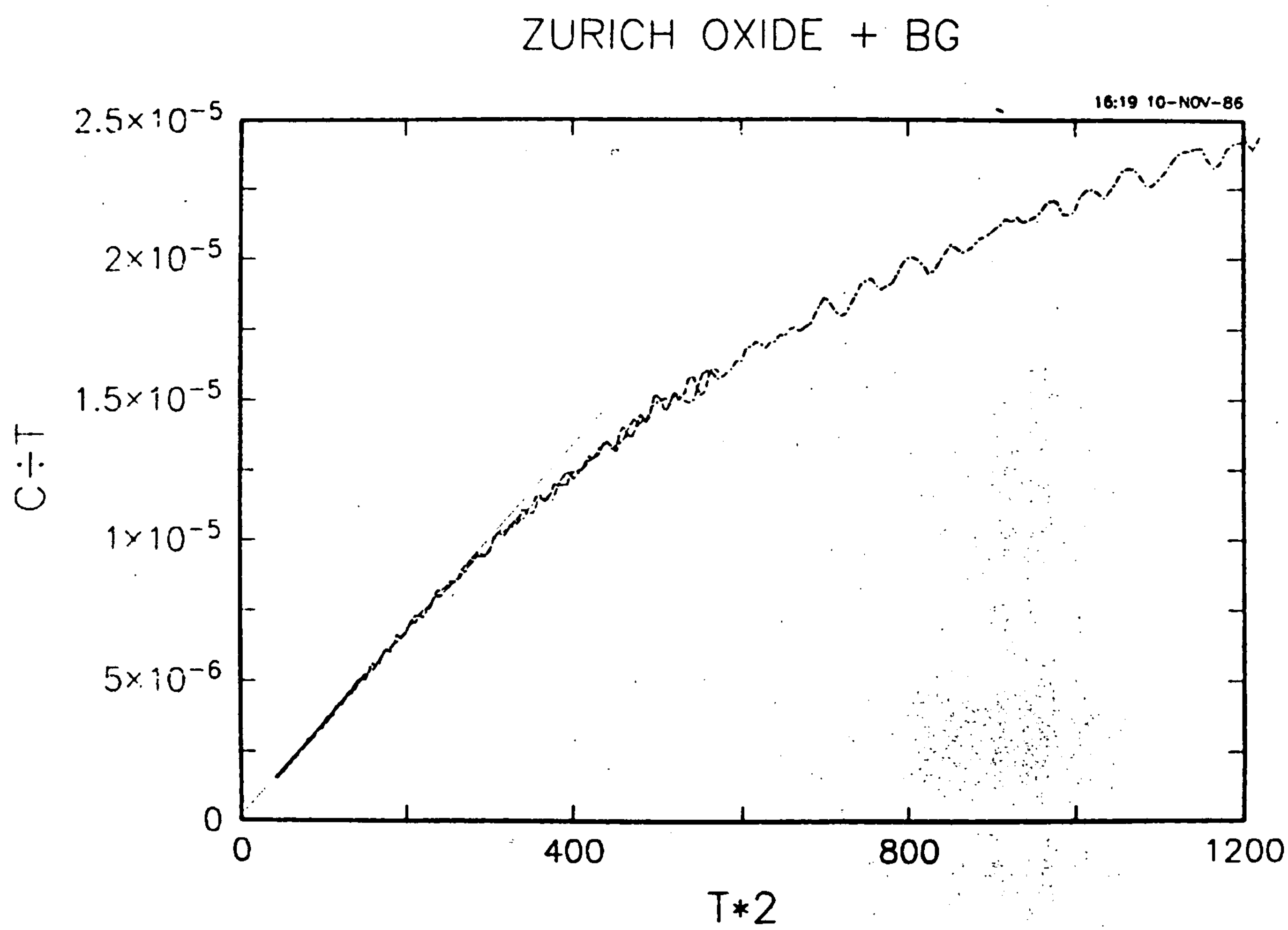
ZURICH OXIDE BLCO21



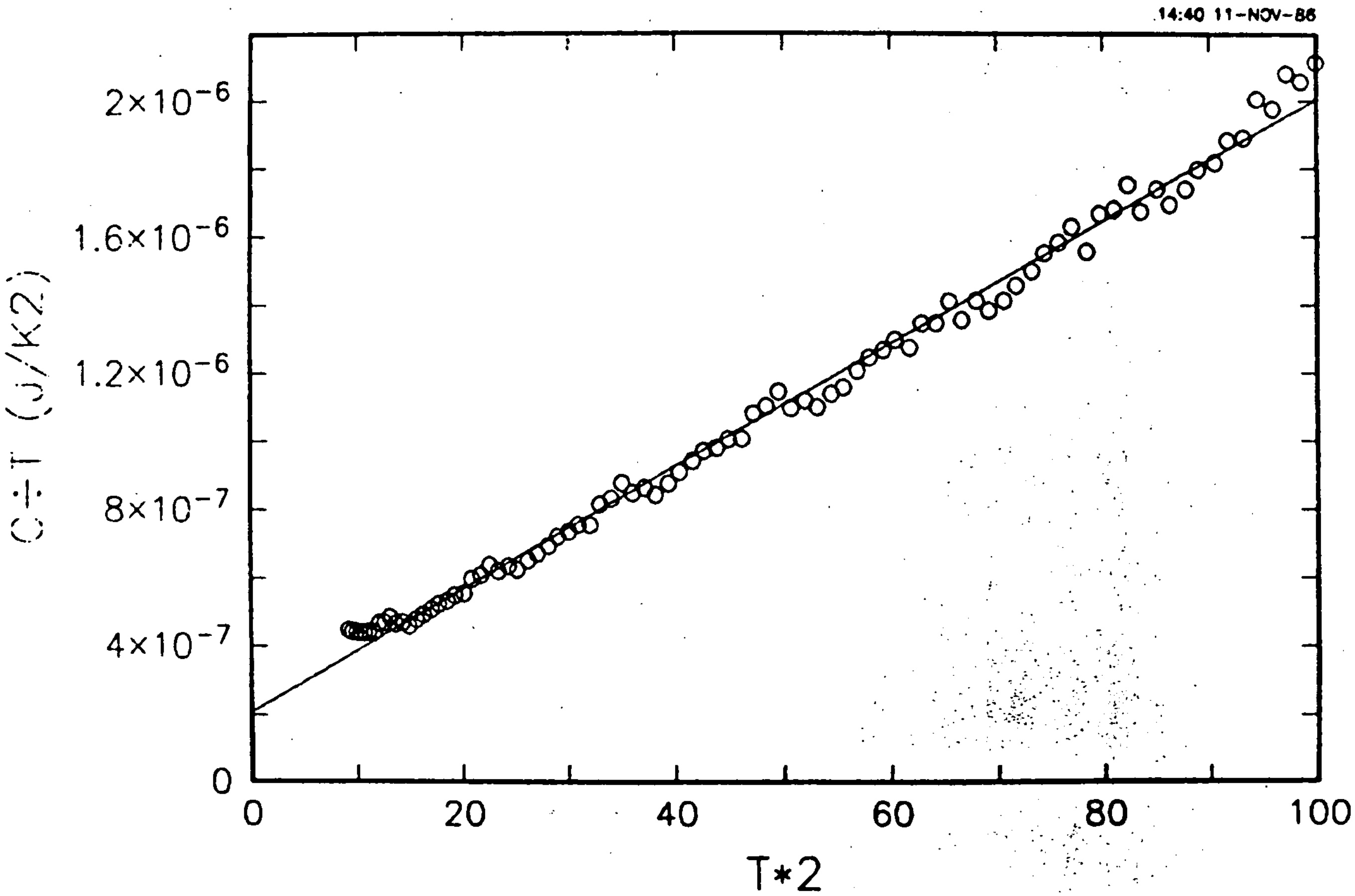
ZO+BG WITH BG



12:19 11-NOV-86
HEAT CAPACITY
3×10⁻⁵
2×10⁻⁵
1×10⁻⁵
0
2
4
6
8
10
TEMPERATURE


ZURICH OXIDE + BG
16:19 10-NOV-86
2.5×10⁻⁵
2×10⁻⁵
1.5×10⁻⁵
1×10⁻⁵
5×10⁻⁶
0
C÷T
0
400
800
1200
T*2

ZURICH OXIDE BLCO21

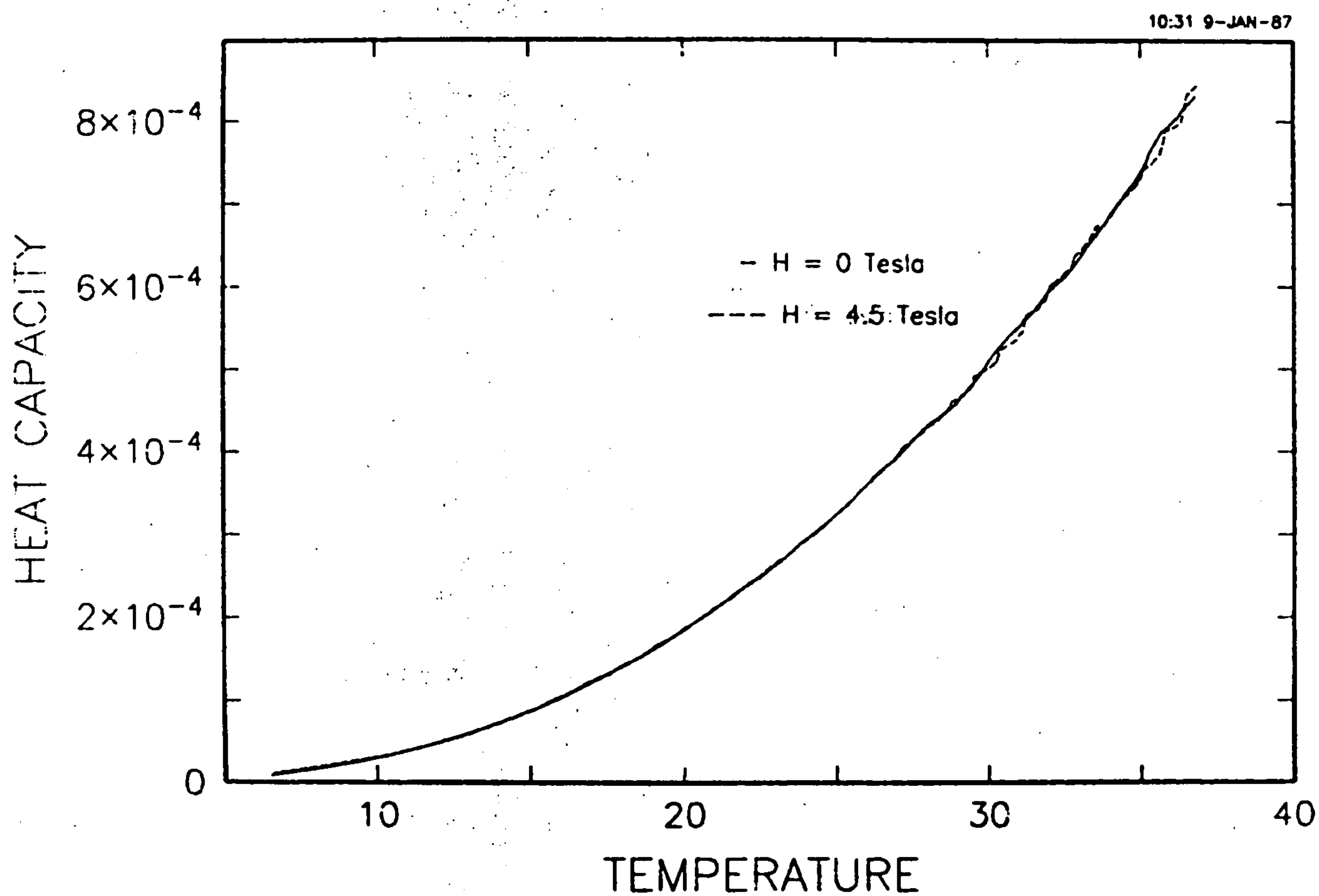


$C = \gamma T + \beta T^3$

$\gamma = 2.08 \times 10^{-7} \, (J/K^2)$

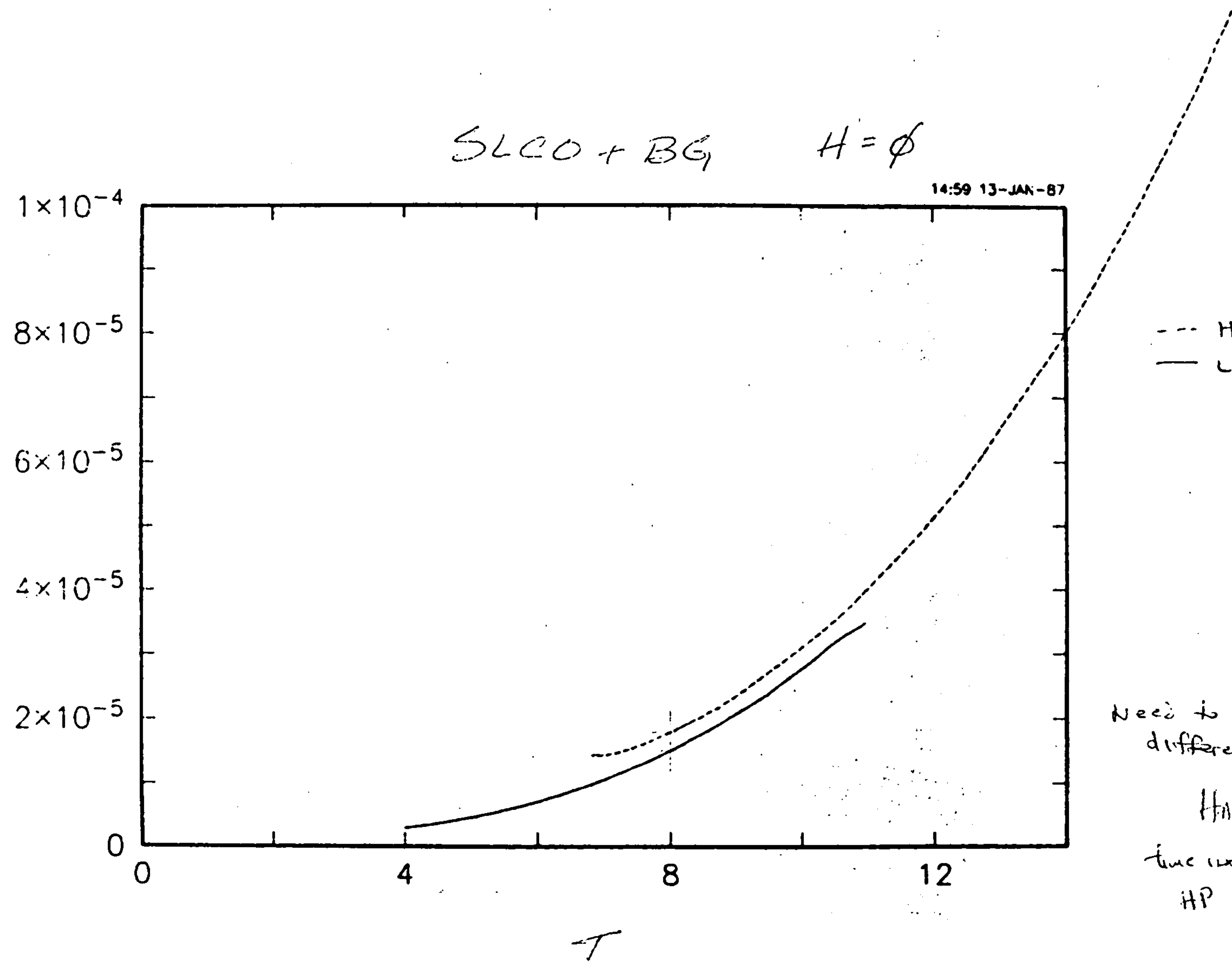
$\beta = 1.80 \times 10^{-8} \, (J/K^4)$

SLCO = 24 mg.



Incorrect RuO_2 Calib- has been redone

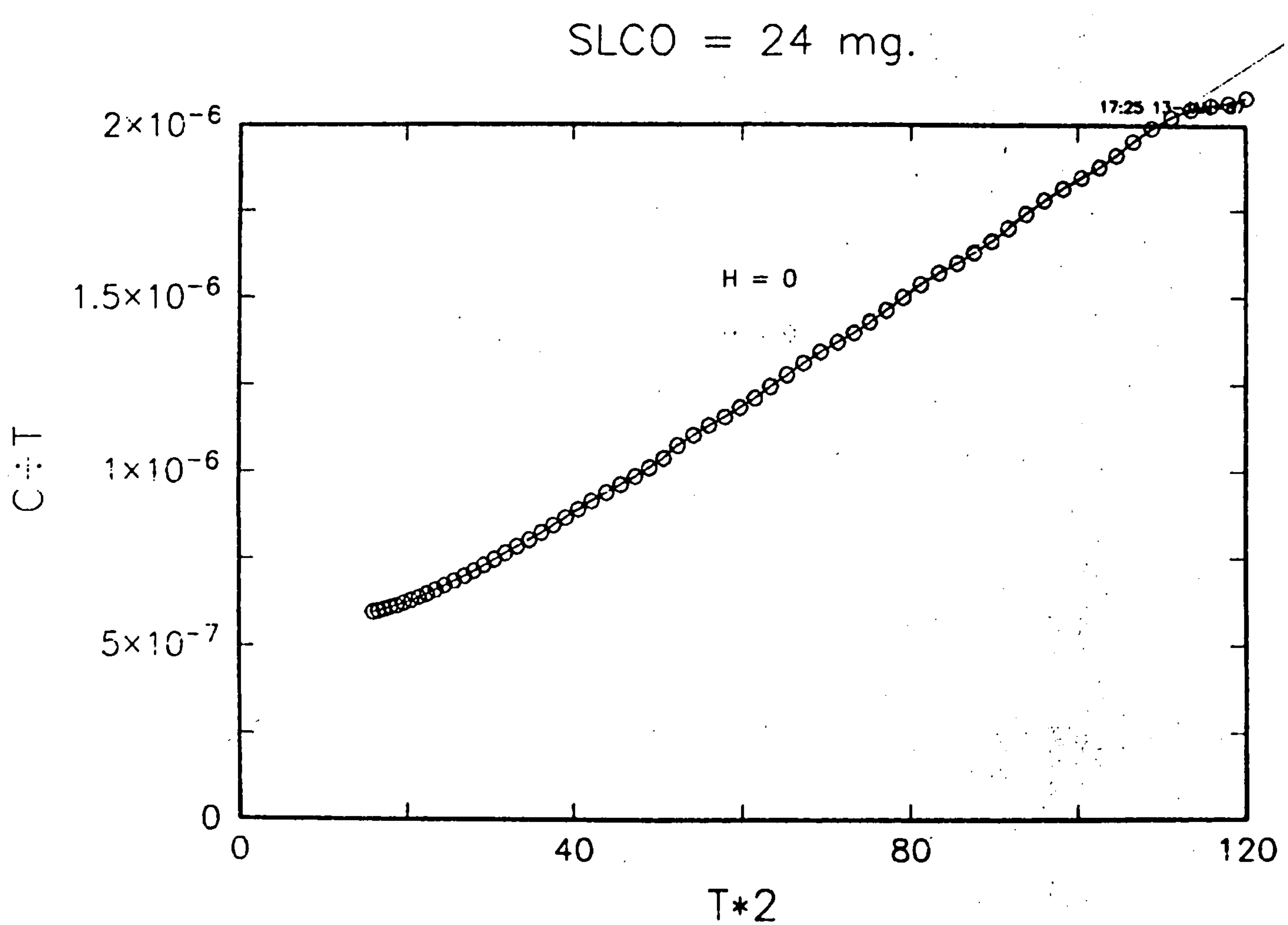
SLCO + BG $H = \phi$

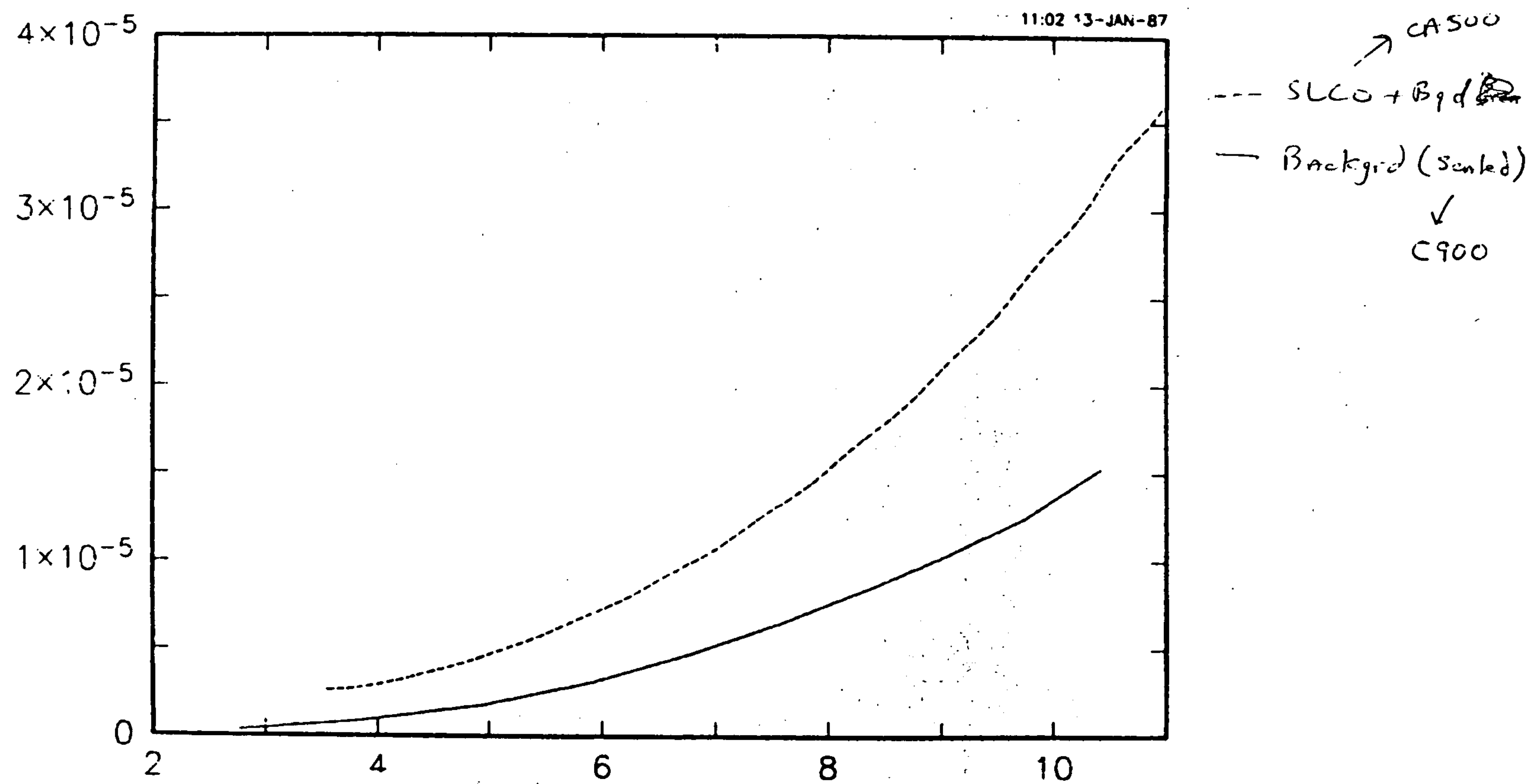


--- HT
— LT   using correct RuO_2 + P(T) calibrations

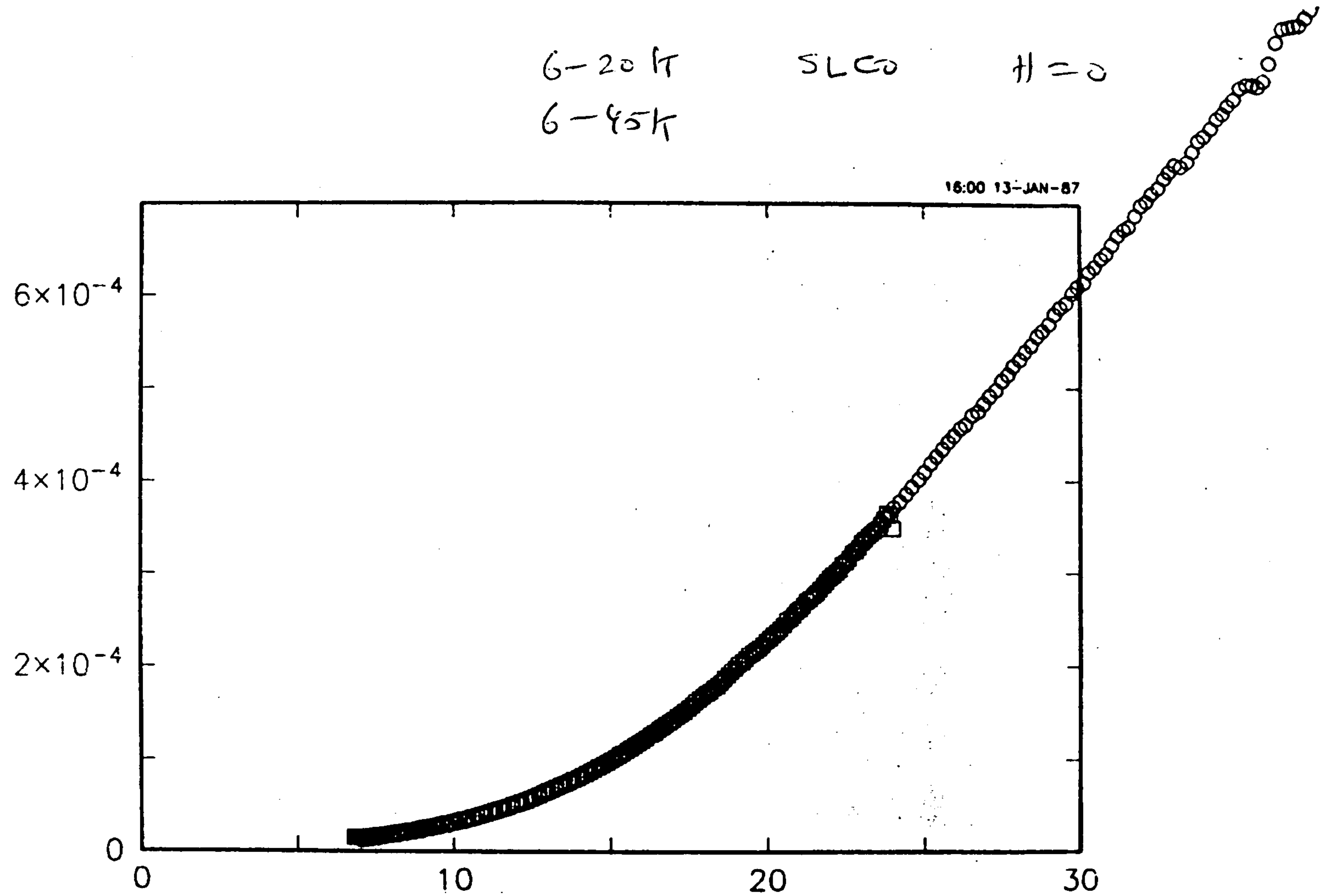
Need to sort out this difference

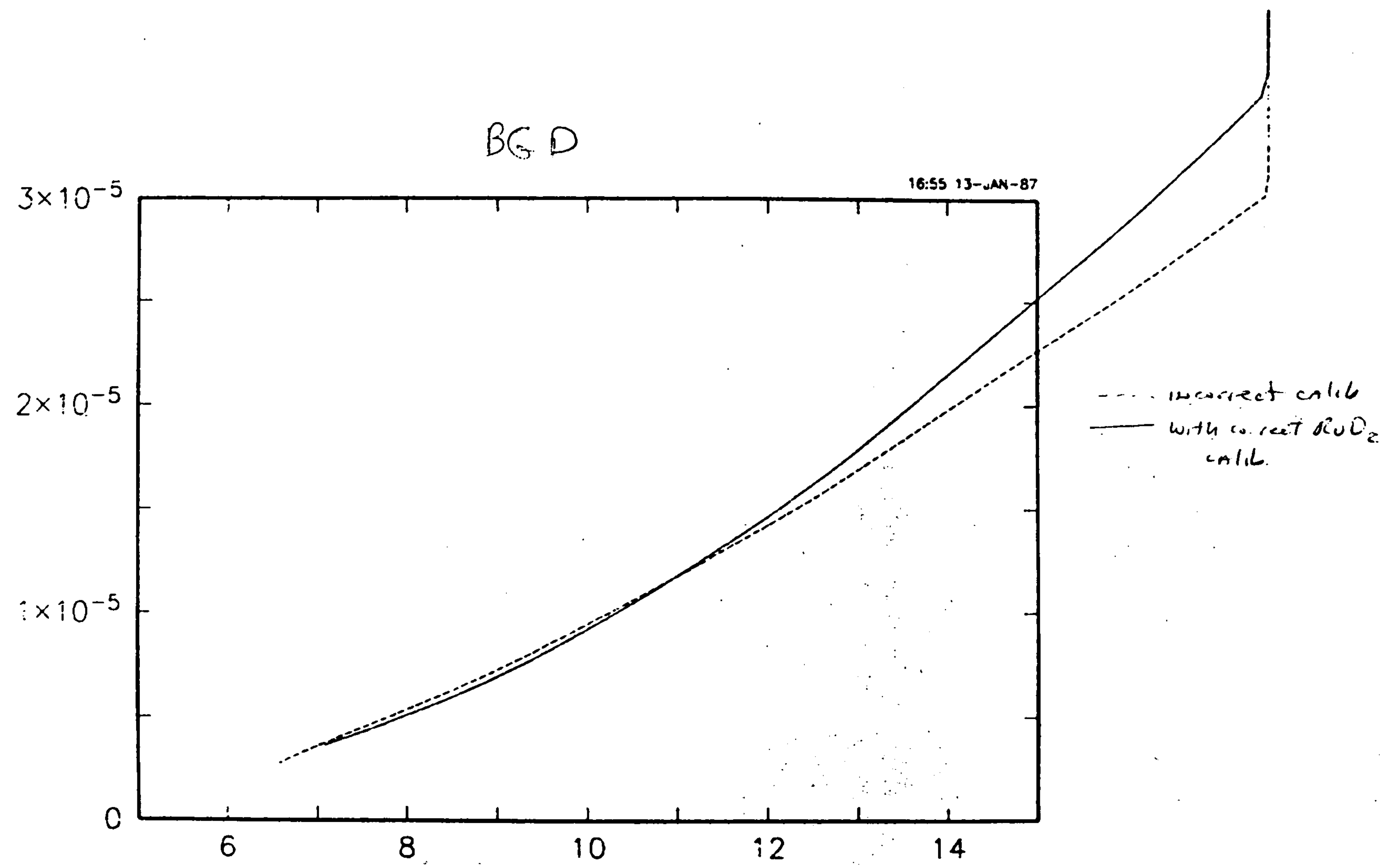
Has been done — time interval problem on HP — see 14 JAN data


SLCO = 24 mg.
H = 0
17:25 13
2×10⁻⁶
1.5×10⁻⁶
1×10⁻⁶
5×10⁻⁷
0
C ÷ T
0
40
80
120
T*2

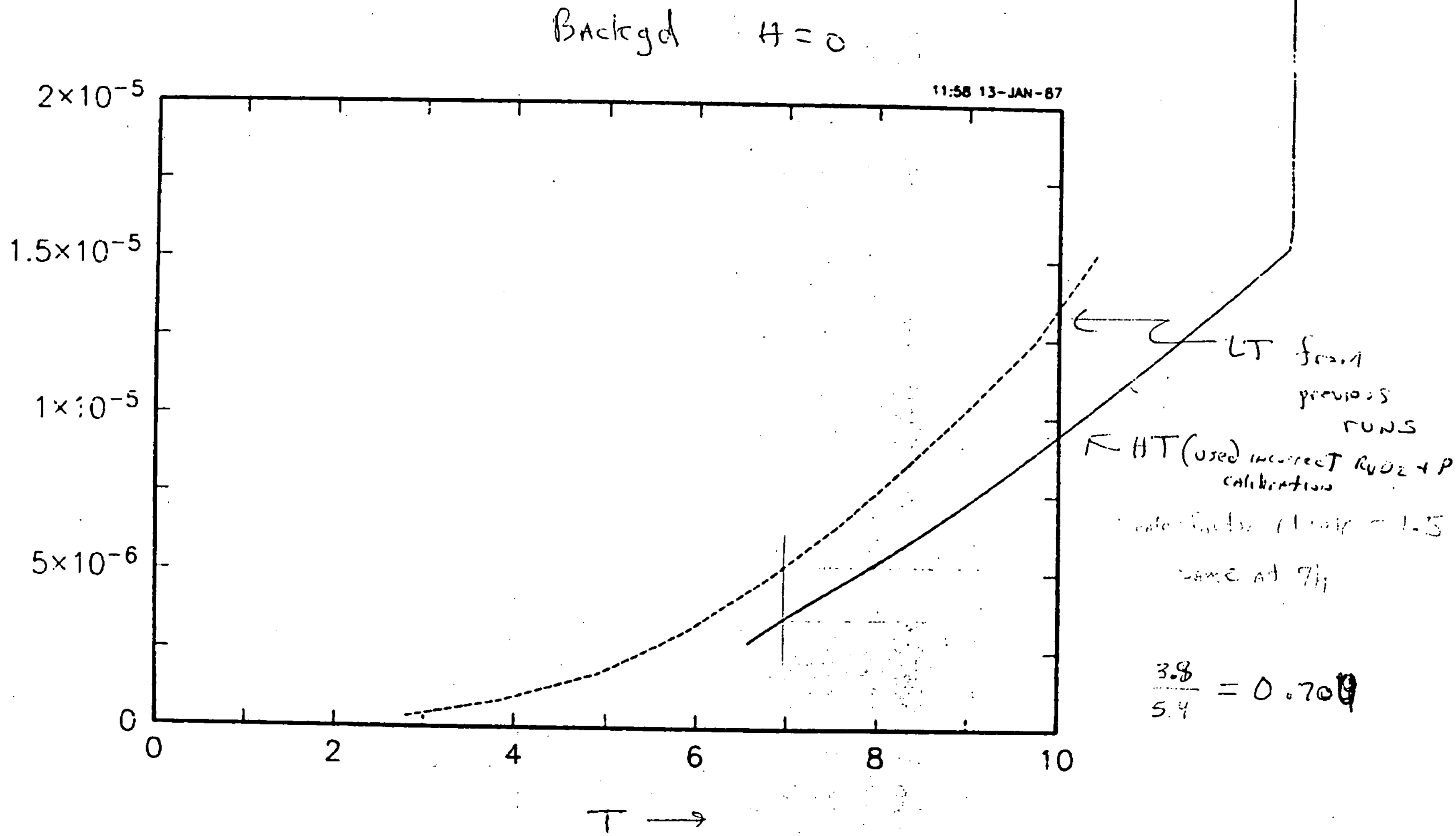

11:02 13-JAN-87
4×10^-5
3×10^-5
2×10^-5
1×10^-5
0
2
4
6
8
10
--- SLCO + Bgd
CA500
— Backgrd (scaled)
C900

6-20 K SLCo H = 0
6-45 K

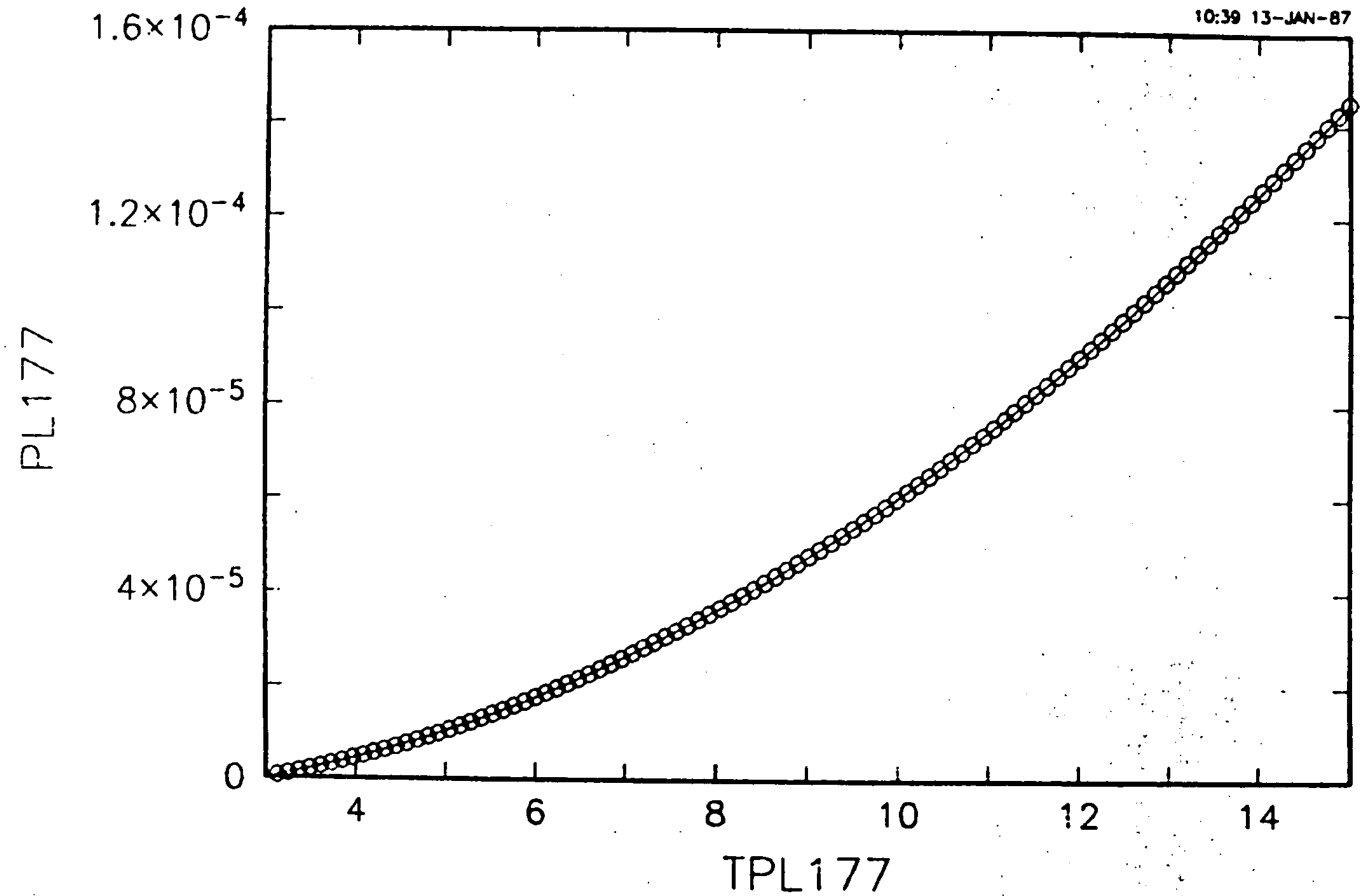


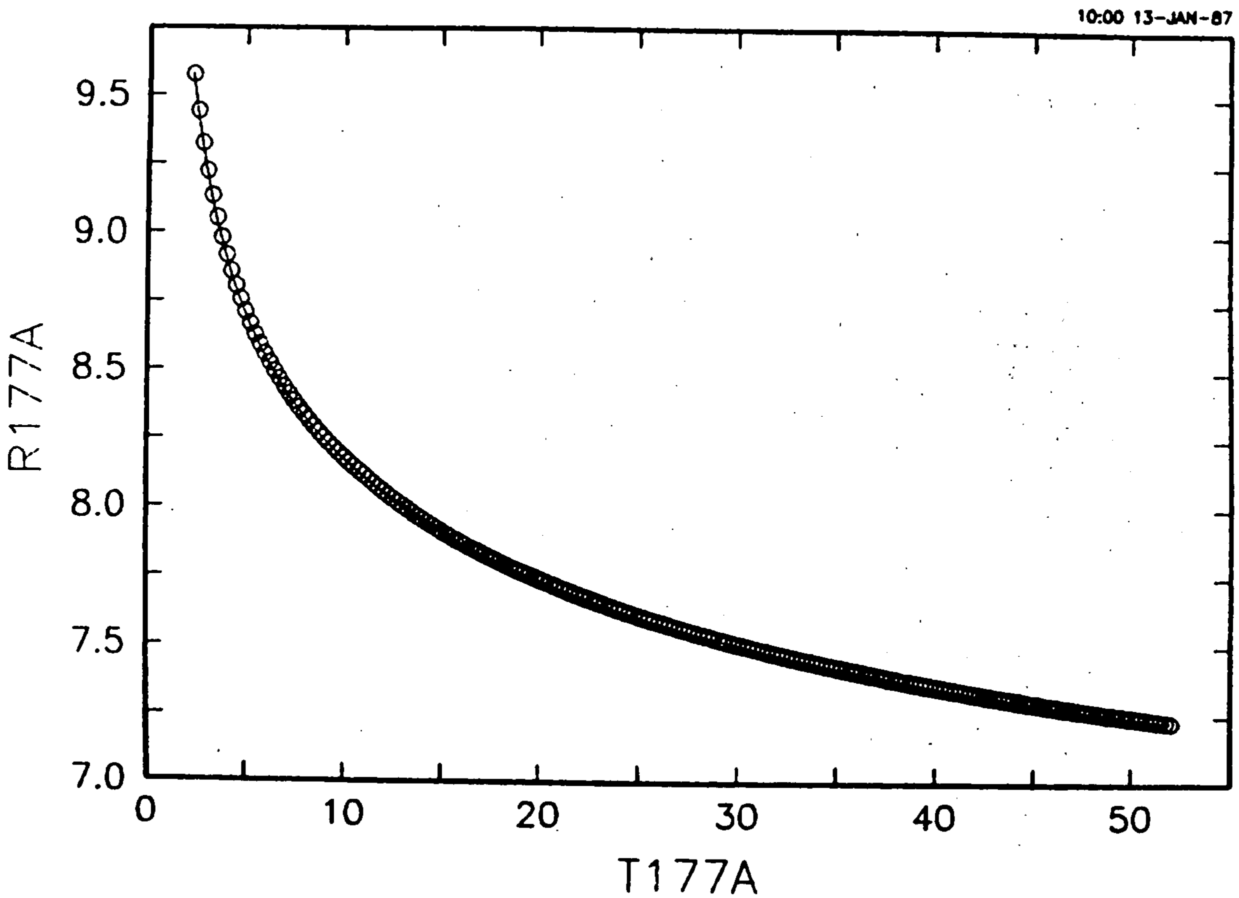


BG D
16:55 13-JAN-87
3×10^-5
2×10^-5
1×10^-5
0
6
8
10
12
14
incorrect calib
with correct RuO2 calib.

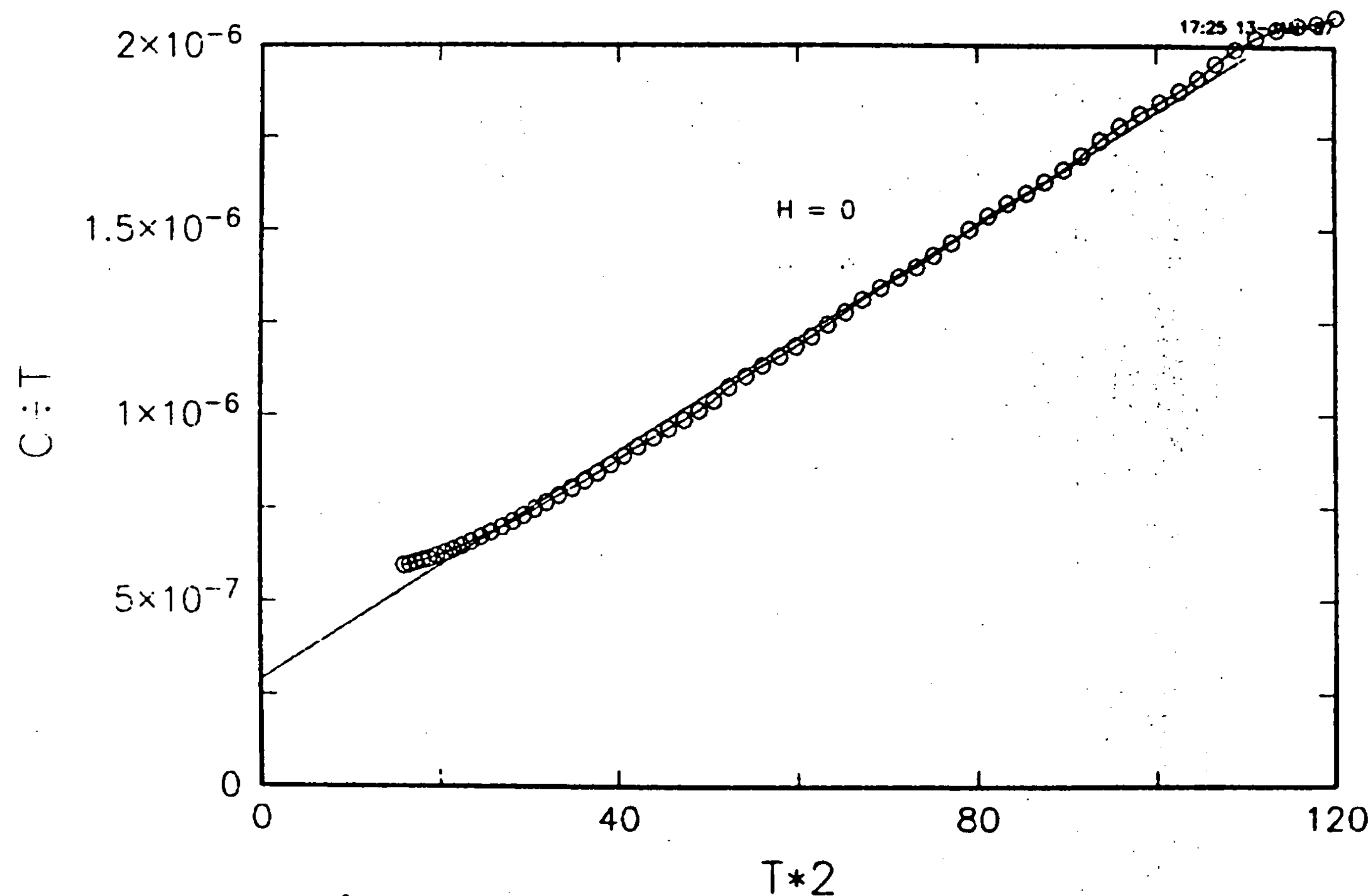


Backgd H = 0
11:58 13-JAN-87
2×10⁻⁵
1.5×10⁻⁵
1×10⁻⁵
5×10⁻⁶
0
0
2
4
6
8
10
T →
LT from previous runs
HT (used incorrect RuO2 + P calibration
3.8/5.4 = 0.70


10:39 13-JAN-87
1.6×10⁻⁴
1.2×10⁻⁴
8×10⁻⁵
4×10⁻⁵
0
PL177
4
6
8
10
12
14
TPL177


10:00 13-JAN-87
9.5
9.0
8.5
8.0
7.5
7.0
R177A
0
10
20
30
40
50
T177A

SLCO = 24 mg.

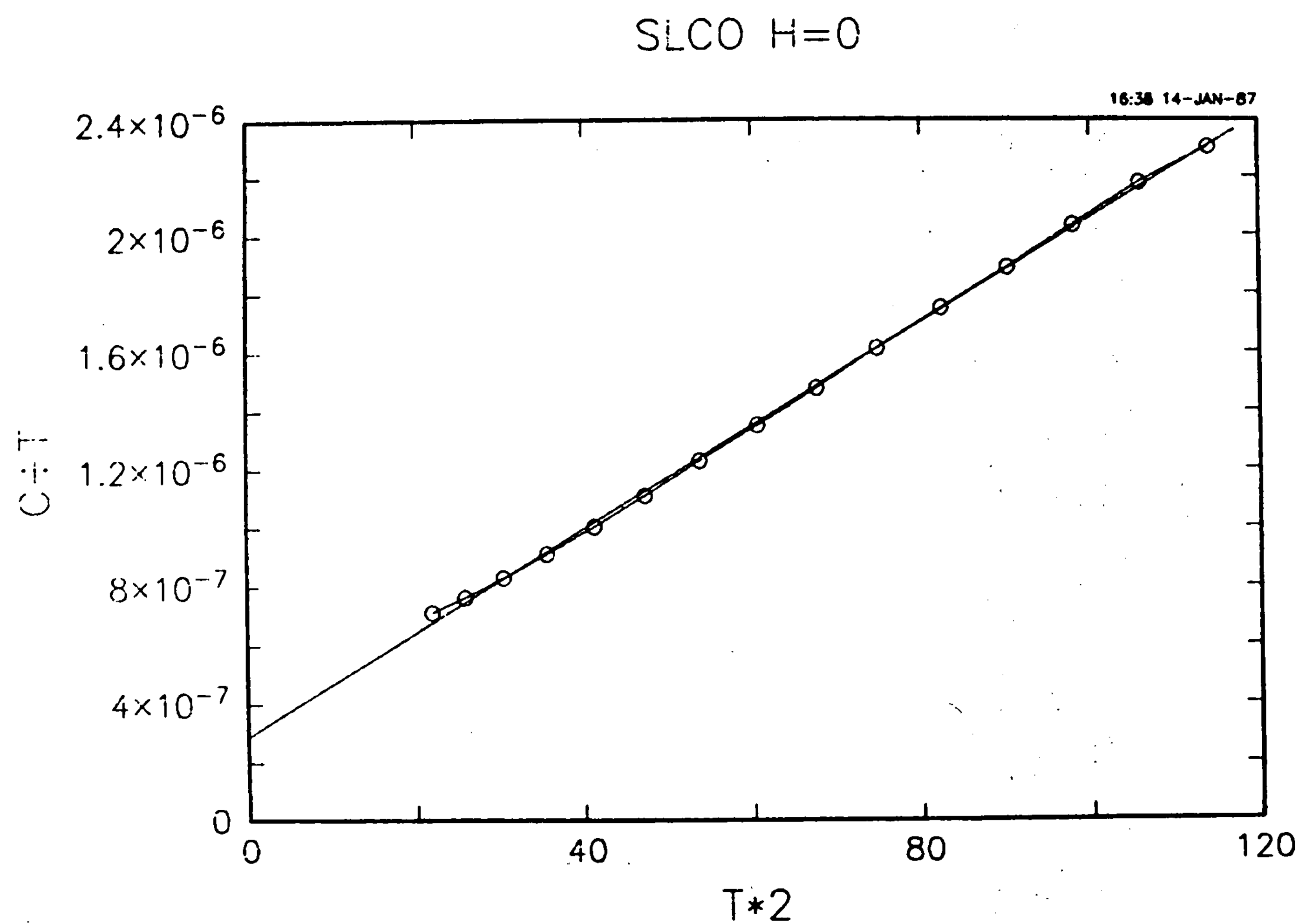


CLS vs TLS

CLS = CA500 - C900

Fit gives $\gamma = 2.92 \times 10^{-7}\ J/K^2$

$\beta = 1.53 \times 10^{-8}\ J/K^4$



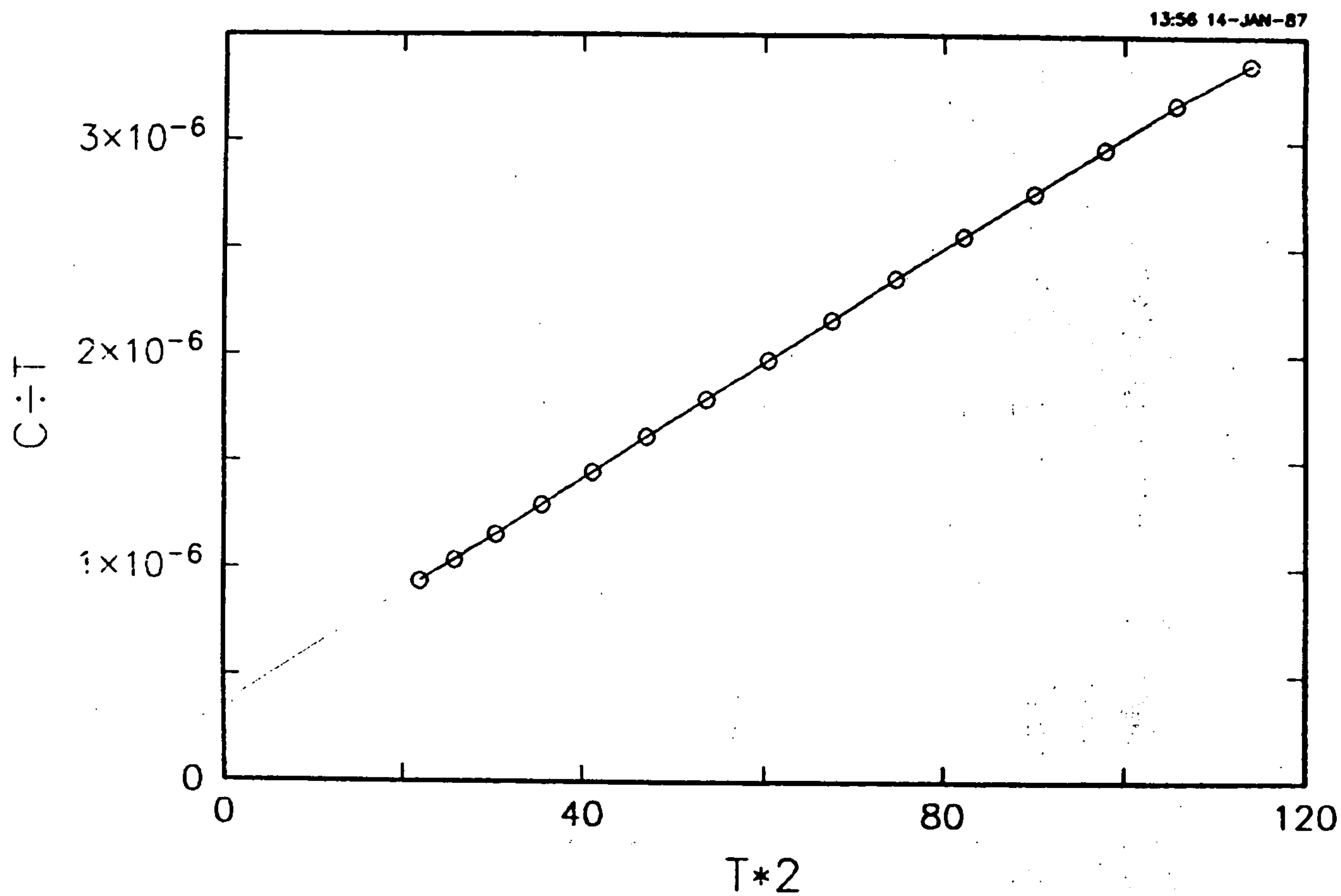
$\gamma = 2.90 \times 10^{-7}$

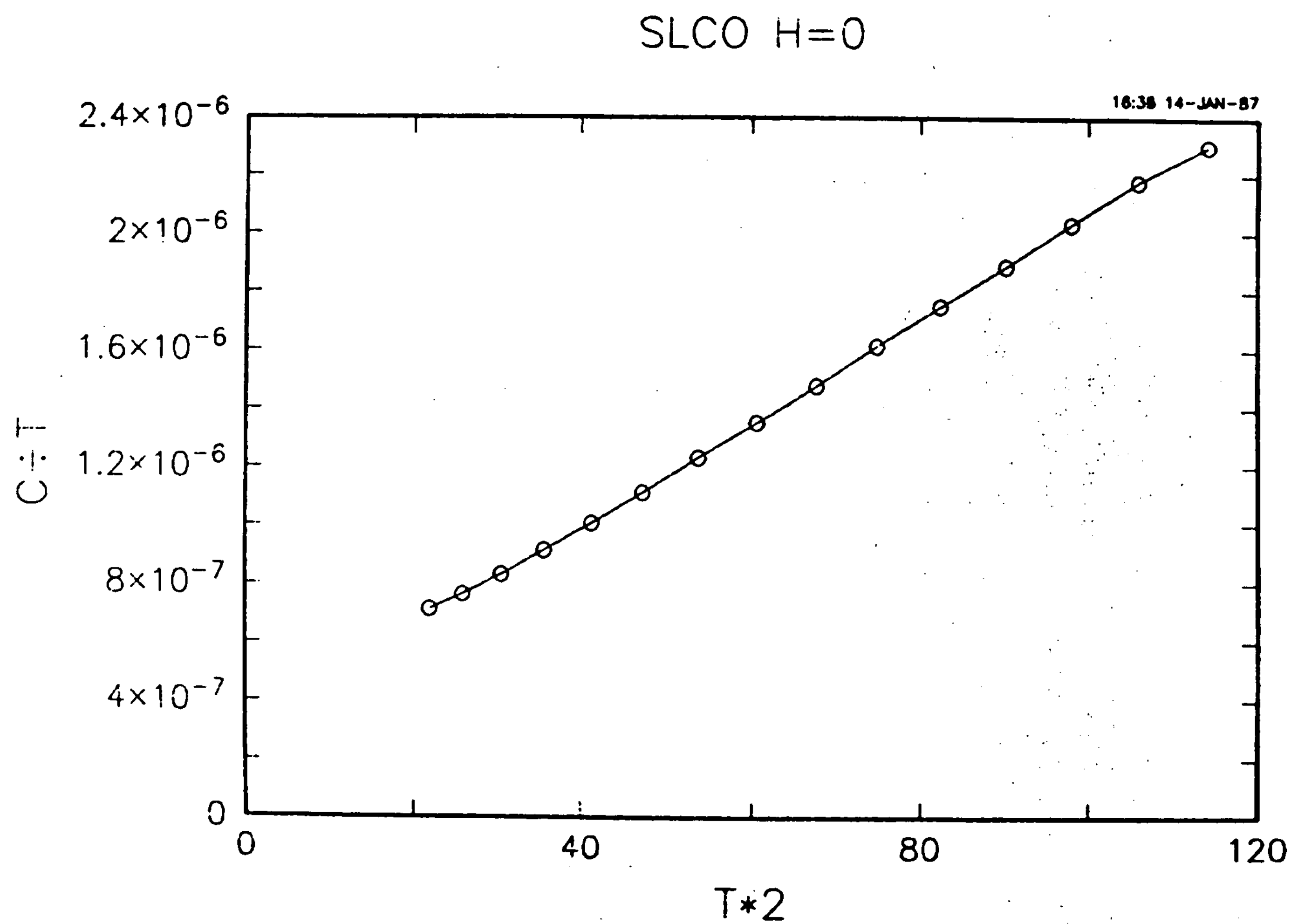
$\beta = 1.77 \times 10^{-8}$

CSLO vs TSL

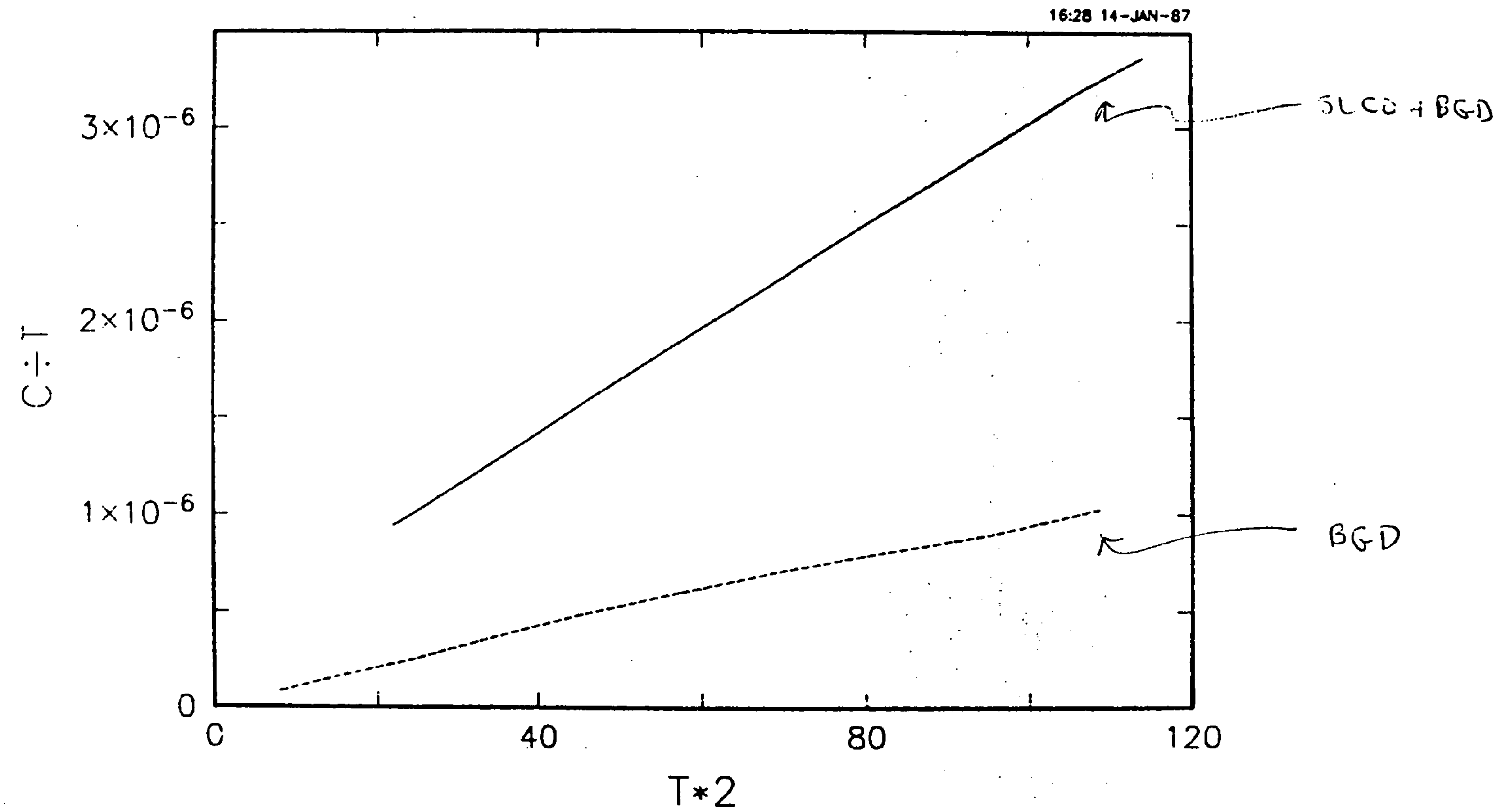
CA114 – C900

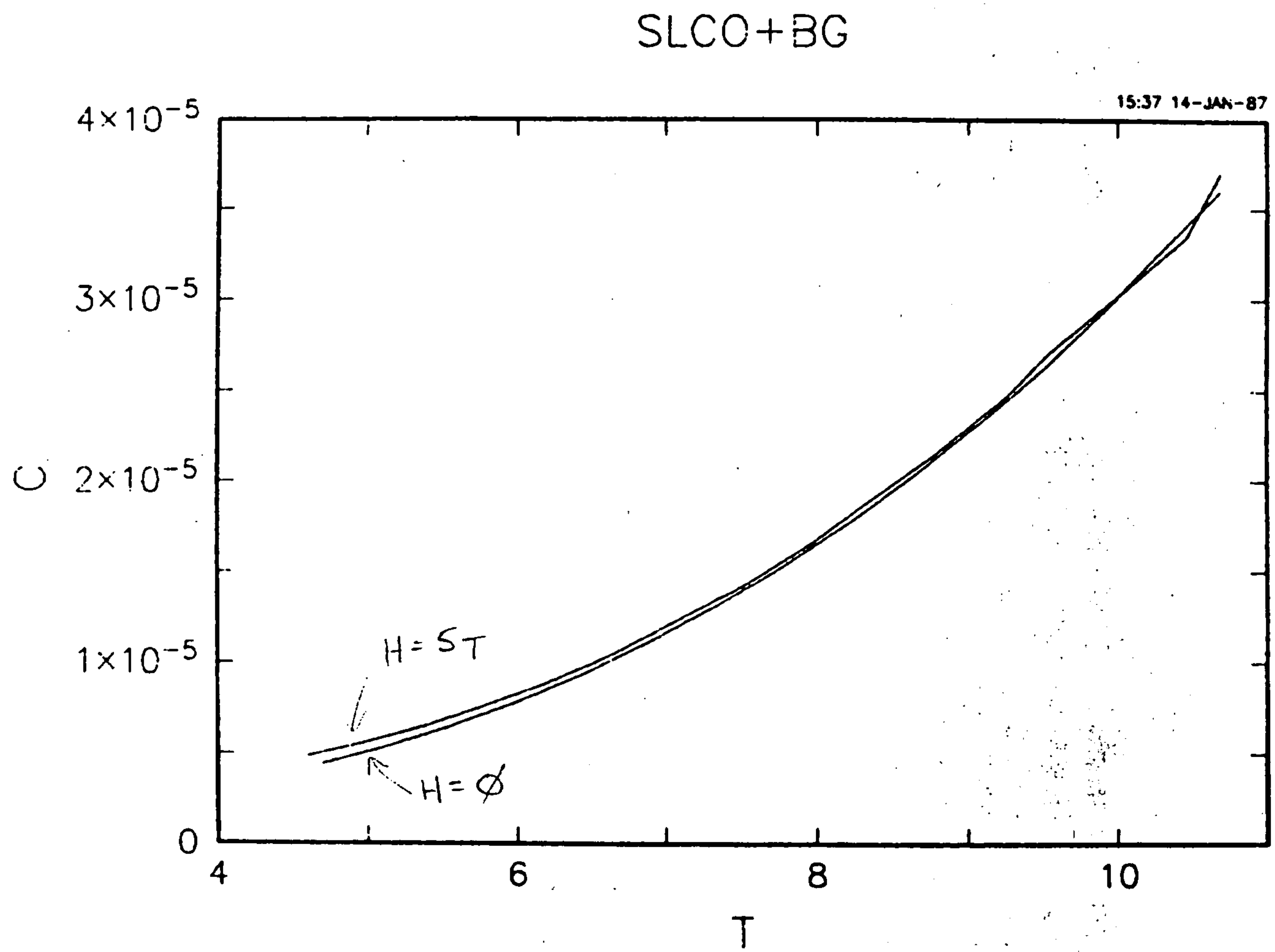
SLCO+BG H=0




SLCO H=0
16:38 14-JAN-87
2.4×10⁻⁶
2×10⁻⁶
1.6×10⁻⁶
1.2×10⁻⁶
8×10⁻⁷
4×10⁻⁷
0
C÷T
0
40
80
120
T*2

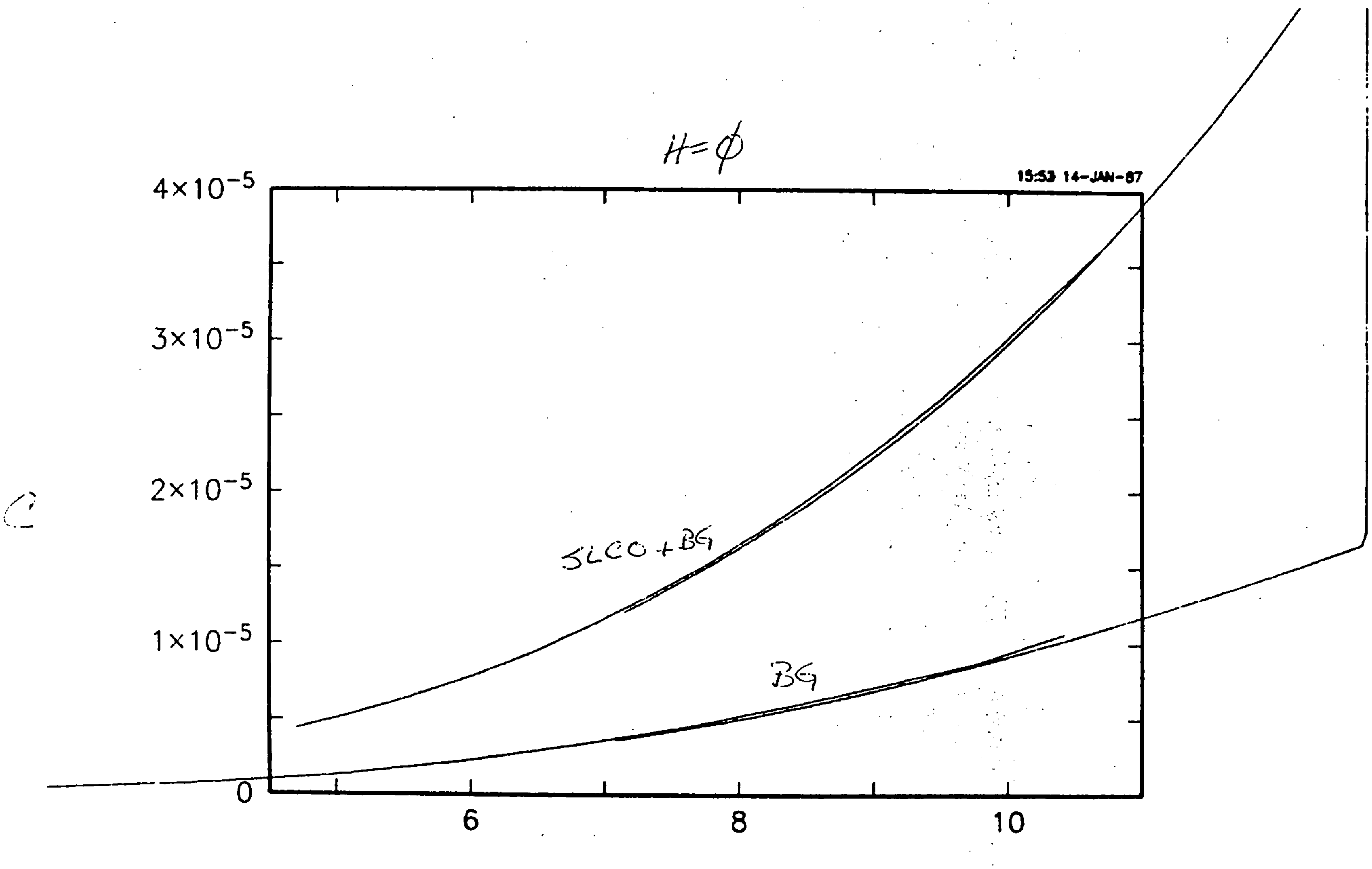
H=0


16:28 14-JAN-87
3×10^{-6}
2×10^{-6}
1×10^{-6}
0
C÷T
0
40
80
120
T*2
5LCO + BGD
BGD



H=ϕ
CA114

H=5T
CA116

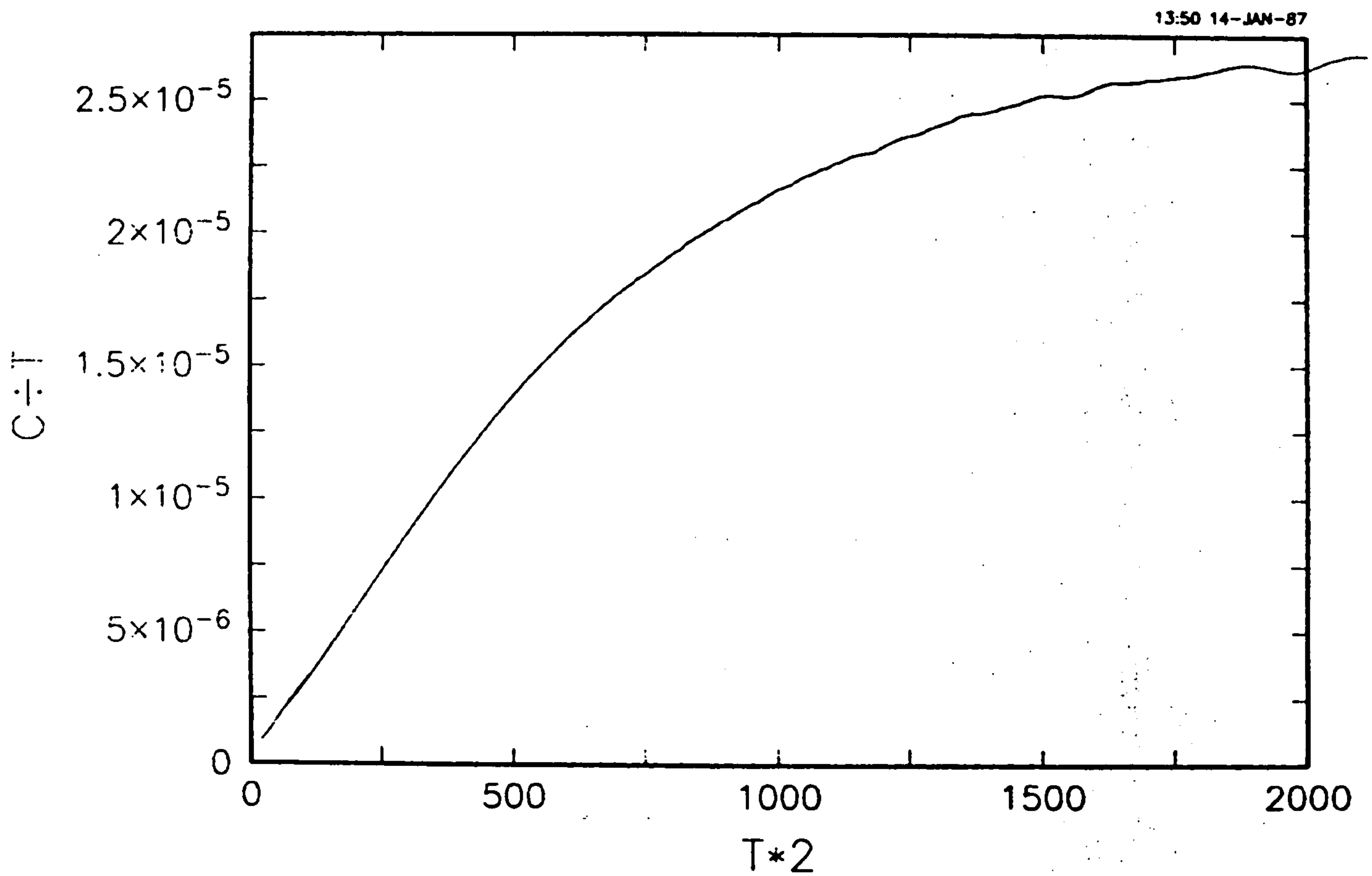


lowT background scaled by 0.7 as on JAN 13

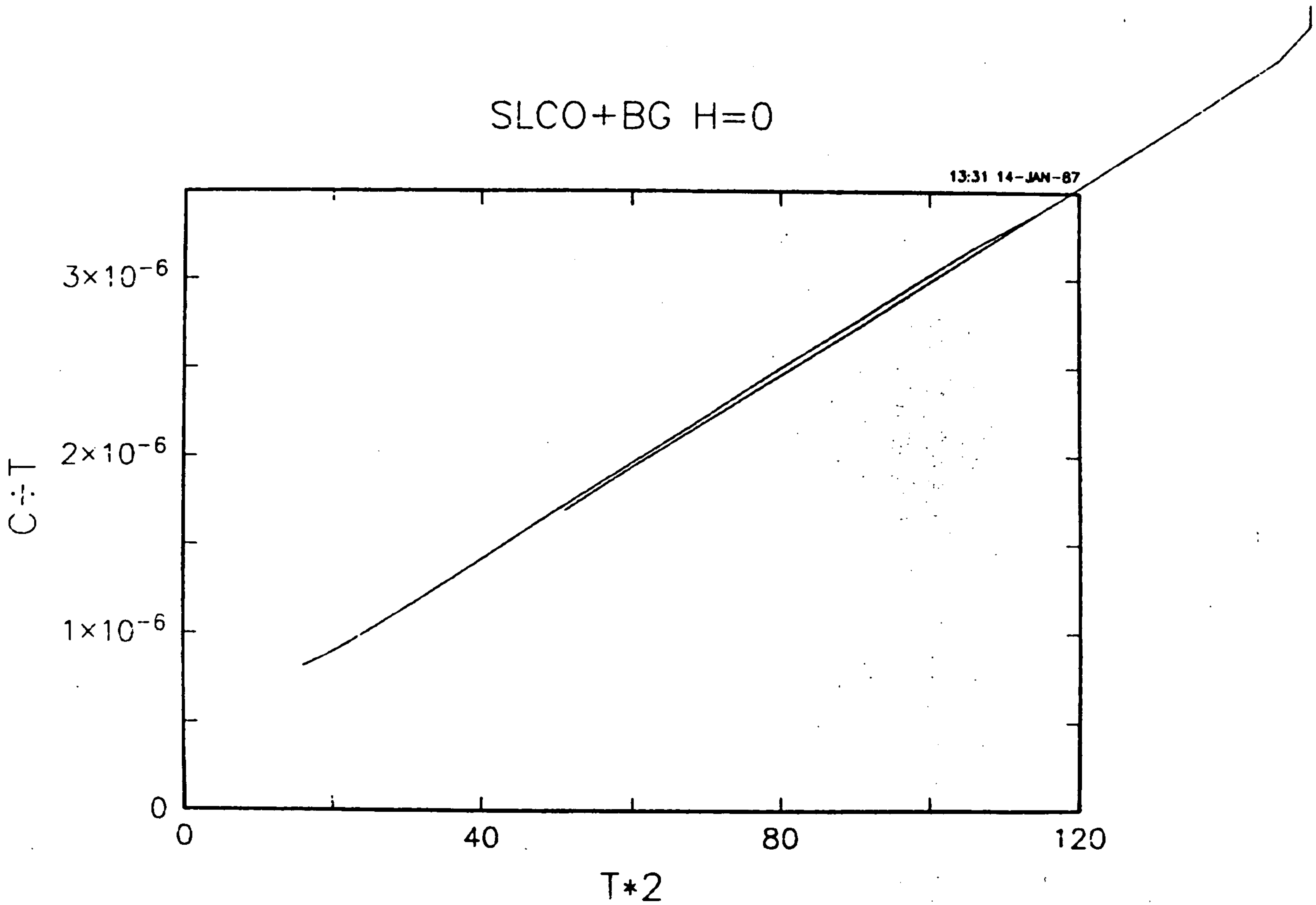
LT SLCO+BG = CA114, TA114
HT SLCO+BG = CA100, TA100

LT BG = C900, T900
HT BG = CA800, TA800

SLCO+BG H=0



LT = CA114
HT = CA222


SLCO+BG H=0
13:31 14-JAN-87
C÷T
3×10⁻⁶
2×10⁻⁶
1×10⁻⁶
0
0
40
80
120
T*2

SLCO+BG H=0